PB-221 485

BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES

John E. Barker, et al

Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma

April 1973

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EPA-R2-73-167
April 1973

Environmental Protection Technology Series

W73-11328

PB 221 485

Biological Removal of Carbon and Nitrogen Compounds from Coke Plant Wastes

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177

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EPA-R2-73-167
April 1973

BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES

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Project 12010 EDY

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OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price $2.35 domestic postpaid or $2.00 GPO Bookstore

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ABSTRACT

A one-year study of a biological process for treatment of coke plant ammonia liquor was conducted. The process was designed to remove carbon compounds and ammonia. The pilot plant consisted of three treatment systems arranged in series. These systems were designed for the removal of carbon compounds, the oxidation of ammonia to nitrate (nitrification), and the reduction of nitrate to nitrogen gas (denitrification). The study was jointly sponsored by the American Iron and Steel Institute, the Environmental Protection Agency, and Armco Steel Corporation.

The results of the study indicate that the biological process can be used to remove carbon compounds and ammonia from dilute ammonia liquor. Treatment efficiencies obtained include removals of greater than 99.9 percent phenol, 80 percent COD and 90 percent ammonia. Removal efficiencies for cyanide and thiocyanate were less encouraging with averages of 57 and 17 percent, respectively. At this time, the inability to efficiently remove cyanide and thiocyanate raises a question as to the long range applicability of the process to existing and proposed water quality standards.

A complete evaluation of the capabilities and limitations of the system was beyond the scope of this study. Additional development work will be required before the process could be considered for commercial application.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. 2.

W 73-11328

Biological Removal of Carbon and Nitrogen Compounds
from Coke Plant Wastes, (all caps)

5. Report Date
6.
8. Performing Organization Report No.

Barker, John E.; Thompson, R. J.~~; Samples, W. R.;~~
~~McMichael, F. C.~~

EPA Project 12010 EDY

American Iron and Steel Institute,
~~150 East 42 Street~~
New York City, New York, ~~10017~~

Type of Report and Period Covered

~~12. Sponsoring Organization~~

15.

Environmental Protection Agency, Technology Series report
~~number,~~ EPA-R2-73-167, April 1973. 178p, 9fig, 23tab, 65ref

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17a. Descriptors

~~Group 16 (WABC)~~ Aerobic Conditions, Anaerobic Condition, Biochemical Oxygen Demand, Heated Water, Industrial Wastes, *Nitrogen Compounds, Organic Matter, Phenols, ~~Water Pollution Sources,~~ *Biological treatment, *Waste water treatment, *Carbon, Activated sludge, Pilot plants

17b. Identifiers

*Coke Plant wastes, Ammonia Liquor, Nitrification, Denitrification, ~~Carbon Compound, Ammonia, Cyanide, thiocyanate, Phenol, State-of-the-Art, Aeration Time, Problem areas~~, ~~Sludge bulking, Activated Sludge, Pilot Plant.~~

17c. COWRR Field & Group 05D, 05B

Copy available from GPO Sup Doc as EP1.23/2:73-167 $2.35; microfiche from NTIS as PB[illegible], $0.95.

18. Availability

19. Security Class. (Report)	21. No. of Pages	**Send To:**
20. Security Class. (Page)	22. Price	WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D.C. 20240

Leon H. Myers

Robert S. Kerr Environmental Research Lab.

CONTENTS

Section		Page
I	CONCLUSIONS AND RECOMMENDATIONS	1
II	INTRODUCTION	5
III	DESCRIPTION OF PROBLEM	7
IV	POTENTIAL SOLUTIONS TO PROBLEM	13
	Modified Method of Coke Production	13
	Quenching	14
	Incineration	14
	Distillation	14 & 15
	Deep Well Disposal	15
	Removal or Recovery of Specific Contaminates	15
V	BIOLOGICAL OXIDATION AND DENITRIFICATION	27
	Biological Oxidation of Coke Plant Wastes	27
	Biological Nitrification and Denitrification	33
VI	DESCRIPTION OF PILOT PLANT	39
VII	SAMPLING AND ANALYSIS	45
VIII	OPERATIONS AND RESULTS	49
	The Excess Ammoniacal Liquor	50
	Carbonaceous Treatment Unit	52
	Nitrification Unit	72
	Denitrification Unit	82
IX	SPECIAL STUDIES	91
	Carbonaceous Unit	91
	Denitrification Unit	94
X	COST ESTIMATES	97
XI	ACKNOWLEDGEMENTS	103
XII	REFERENCES	105
XIII	PUBLICATIONS	111
XIV	GLOSSARY	113
XV	APPENDIXES	

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FIGURES

No.		Page
1	FLOW DIAGRAM BY-PRODUCT COKE PLANT	9
2	HYPOTHETICAL PATHWAYS OF NITRATE REDUCTION IN MICRO-ORGANISMS	35
3	PILOT PLANT FLOW DIAGRAM	41
4	SAMPLING POINT LOCATIONS	46
5	CARBON REMOVAL UNIT-PERCENTAGE OF WASTE UNDER TREATMENT	57
6	CARBON REMOVAL UNIT-INFLUENT CONCENTRATIONS, ORGANIC CARBON AND COD	59
7	CARBON REMOVAL UNIT-INFLUENT CONCENTRATIONS, PHENOLICS	60
8	CARBON REMOVAL UNIT-INFLUENT CONCENTRATION, THIOCYANATE	61
9	EXCESS AMMONIA LIQUOR-CONCENTRATIONS, TOTAL NITROGEN AND AMMONIA	62

TABLES

No.		Page
1	TYPICAL QUANTITIES OF VOLATILE PRODUCTS PER TON OF COKE	8
2	TYPICAL ANALYSIS OF AMMONIACAL LIQUOR AND STILL WASTE	10
3	PILOT PLANT EQUIPMENT	42
4	SAMPLING AND ANALYSIS SCHEDULE	47
5	EXCESS AMMONIACAL LIQUOR	51
6	SUMMARY OF CHARACTERISTICS - EXCESS AMMONIACAL LIQUOR	52
7	OPERATING CONDITIONS, CARBON REMOVAL UNIT	54
8	INFLUENT, CARBON REMOVAL UNIT	55
9	LOADINGS AND REMOVALS, CARBON REMOVAL UNIT	56
10	EFFLUENT LOADS PER UNIT VOLUME OF WASTE	66
11	SUMMARY OF CONDITIONS DURING PERIODS OF UNIT STABILITY	70
12	SUMMARY OF TREATMENT UNIT FAILURES	71
13	OPERATING CONDITIONS, NITRIFICATION UNIT	74
14	NITRIFICATION UNIT, SUMMARY	77
15	OPERATING CONDITIONS, DENITRIFICATION UNIT	78
16	OPERATING RESULTS, DENITRIFICATION UNIT	85
17	DENITRIFICATION - STOICHIOMETRIC COMPUTATION	87
18	PRETREATMENT OF EXCESS AMMONIACAL LIQUOR, PERCENT REMOVALS	92
19	BIOLOGICAL REMOVALS FROM PRETREATED WASTE	93
20	CAPITAL COST E.A.L. BIOLOGICAL TREATMENT	98
21	OPERATING COST BIOLOGICAL TREATMENT	100
22	COST COMPARISONS OF NITRIFICATION CHEMICAL REQUIREMENTS	101
23	COST COMPARISON OF ORGANICS FOR DENITRIFICATION	102

SECTION I

CONCLUSIONS AND RECOMMENDATIONS

After nearly one year of pilot plant operation, it is concluded that carbon compounds can be biologically removed from diluted ammonia liquor. Although this project demonstrates that ammonia can be partially removed by biological oxidation, it failed to demonstrate consistent removal of ammonia to the degree necessary for the effluent standards, currently under consideration by regularoty authorities. The cost per unit of ammonia removal compared to other processes casts doubt on the commercial feasibility of this aspect of the process. Three stages of treatment are required. These treatment stages are carbon removal, nitrification and denitrification. The three biological processes must be arranged in this order if effective treatment is to be achieved.

Unanticipated delays and system upsets caused primarily by rapid fluctuations in ammonia liquor strength prevented the complete evaluation of important process requirements particularly for the nitrification system. Some of the more important parameters not completely defined are waste loading, temperature, and sludge wasting requirements. These parameters have a significant effect on the size, efficiency, and cost of biological treatment systems. Additional development to evaluate and define the effect of these design parameters will be required before the system could be considered for commercial application.

Several specific observations and conclusions were made during the study. These are as follows:

1. The strength of ammonia liquor is highly variable. Fluctuations by factors of three or more in concentration of many constituents were not uncommon. This variability must be eliminated or dampened if stable and efficient biological treatment is to be achieved.

2. Utilizing an aeration time of 24 hours and temperatures between 75 and 90°F, the carbonaceous removal unit treated diluted excess raw ammonia liquor at influent concentrations of chemical oxygen demand of 3000 mg/l and phenolics of almost 600 mg/l. Removals of essentially all of the phenolics and about three-quarters of the COD were experienced. Operation is improved by the higher temperatures.

3. Thiocyanate, a major component of ammonia liquor, was only partially removed by the carbonaceous removal unit even at very low unit loadings. Apparently, during most of the experiment conditions were not conducive to the proliferation of organisms capable of oxidizing thiocyanate. Residual thiocyanate in the carbonaceous units effluent is a major contributor to residual COD.

4. Cyanide removal was quite erratic with removal efficiencies averaging only 57 percent. Fluctuations in cyanide removal were generally unpredictable and inconsistent with waste strength.

5. At low unit loadings, significant nitrification of ammonia was measured in the carbonaceous treatment stage.

6. During one part of the study, the carbonaceous unit efficiently removed COD and phenol while operating in a mode similar to an aerated lagoon.

7. The carbonaceous unit experienced aerator foaming problems which increased with increasing waste strength. Tributyl phosphate was an effective control.

8. Major problems encountered by the carbonaceous unit included variability of loadings resulting from inconsistencies in the raw waste, both high and low reactor temperatures, high reactor cyanide and thiocyanate concentrations, and low reactor dissolved oxygen levels.

9. Nitrifying organisms are quite sensitive to many constituents in ammonia liquor. Dilution and efficient operation of the carbonaceous unit are necessary to prevent inhibition and loss of nitrification efficiency.

10. Nitrification efficiency reached 90 percent oxidation of ammonia when the waste was diluted to 12 percent strength and the carbon removal unit was operating satisfactorily.

11. Additions of agents to supply inorganic carbon for metabolism of the autotrophic nitrifiers and an alkaline agent to neutralize the acidity produced in the process are necessary. The most practical chemical system is sodium carbonate and hydrated lime.

12. Nitrification was found to proceed satisfactorily within the pH range of 6.8 to 8.2 and that temperatures of 90-95°F were much better than 80-85°F.

13. The maximum observed rate of increase in oxidized nitrogen was 150 mg/l of nitrogen per day. This may give some measure of the rate of response of the unit to increases in influent ammonia concentration.

14. The major operational problems of the unit resulted from poor quality carbonaceous unit effluent, high nitrification unit pH and low nitrification unit temperature.

15. The major biochemical reactions occurring within the nitrification unit lead to the oxidation of ammonia to nitrite and nitrate, the reduction of oxygen, and the reduction of carbon dioxide.

16. No overall loss of nitrogen took place within the first two operational units of the pilot plant.

17. The denitrification unit was capable of removing 95 to 100 percent of the oxidized nitrogen at influent concentrations up to 600 ppm.

18. Temperature variations between 70 and 90°F had no observable effect on denitrification efficiency.

19. Alkalinity and pH control were not necessary at oxidized nitrogen removals up to 600 ppm.

20. Sludge bulking in the denitrification unit final clarifier was a problem. Flotation should be considered for solids separation in this system.

21. Molasses proved to be an acceptable reducing agent for denitrification. Dean, et al, has suggested methanol as a reducing agent. From an economic standpoint, methanol which costs twice as much as molasses is considered second choice.

22. Careful control must be exercised to maintain a reasonable balance between oxidized nitrogen and the reducing agent. The recommended dosage of reducing agent in terms of mg/1 of chemical oxygen demand was found to be equal to about 9 times the sum of the milliequivalents per liter of nitrite and nitrate to be reduced.

23. The complete three-stage treatment plant under optimum operating conditions should be capable of removing well over 99 percent of the phenolics, 90 percent of the organic carbon, 70 percent of the chemical oxygen demand, and 90 percent of the ammonia.

24. Preliminary estimates for a treatment system sized for a 33,000 TPM coke plant are $995,000 capital cost and $230,500 annual operating cost. The operating cost represents $15.78 per 1,000 gallons of excess ammonia liquor or $0.58 per net ton of coke. Seventy to eighty percent of this cost is for ammonia removal.

The results of this study strongly suggest that a full-scale biological system to remove carbon compounds from excess ammonia liquor could be designed and built. It also indicates that additional development is required to enable the construction and operation of a reliable, full-scale, biological system for removal of the ammonia.

It is recommended that future research and development efforts be directed at defining the causes and developing methods to eliminate the rapid fluctuations in ammonia liquor strength; defining the parameters required for biological removal of cyanide and thiocyanate, and optimizing the system for their removal; and evaluating the aerated lagoon as an alternate to the activated sludge process.

SECTION II

INTRODUCTION

The operation of by-product coking facilities results in the discharge of nutrients, oxygen consuming materials, and toxic substances to the nation's lakes and streams. This is one of the major unsolved water pollution problems facing the steel industry. The problem is magnified by the concentration of coke production in small areas of the United States. Seventy percent of the producing facilities are located in the states of Pennsylvania, Indiana, Ohio, and Alabama. An additional 20 percent are distributed among five northeastern states. And the remaining 10 percent are scattered across the country in widely-separated locations. The large production of coke, the concentration of coking facilities, and the increasing requirements for water pollution control necessitate the development of a practical method for the treatment of coke plant wastes. Although a considerable amount of research has been conducted, the complexity of the wastes has prevented the development of a practical disposal technique.

Recognizing the need for a practical method for the disposal of coke plant waste, the American Iron and Steel Institute (AISI) initiated a laboratory study in 1968 to determine the applicability of biological treatment to this problem. The AISI Water Resources Fellowship at Carnegie-Mellon University were responsible for this study. From the beginning, it was recognized that several treatment stages would be required. These stages would include carbonaceous removal, nitrification, and denitrification. The treatment stages were arranged in this order to prevent inhibition of the nitrifying bacteria by excessive amounts of organic carbon. Preliminary results from the laboratory pilot plant study were quite encouraging with excellent removals of phenol and ammonia.

On the basis of these preliminary laboratory results, it was decided to conduct a field scale pilot plant study concurrent with the laboratory study. The principal objectives of the study were to determine the technical and economic feasibility of biological treatment of excess ammoniacal liquor. In addition, the effect of various controllable parameters on process efficiency were to be evaluated.

The pilot plant was built at Armco Steel Corporation's Houston, Texas Works. At this location, an existing by-products coke plant supplied a continuous source of waste. The pilot plant was designed as three completely mixed activated sludge plants in series with a maximum capacity of one gallon per minute. The system started operation in January, 1970 and the study was terminated in January, 1971. The results of this one year pilot study including the results of the concurrent laboratory study are presented in this report.

SECTION III

DESCRIPTION OF PROBLEM

Coke is a necessary intermediate product in the manufacture of steel. The importance of coke in steel production is derived from its strength as a reducing agent, its physical characteristics, and its low cost. Coke is used as a reducing agent in the blast furnace where iron ore is converted to molten iron or "hot metal." The hot metal is further refined in open hearth, basic oxygen, or electric furnaces to steel.

The present United States coke production is approximately 60 million tons annually. This production is expected to increase essentially at the same rate as steel production, at least during the next one to two decades. At present, more than 98 percent of all United States coke or 59 million tons annually is produced in by-product coke ovens.

The coking operation may be described as a process for the destructive distillation of coal to produce a coke with satisfactory chemical and physical properties for use in metallurgical applications.

The by-product coke oven is a long and narrow chamber, built in batteries usually consisting of 10 to 100 ovens. The ovens are heated by the combustion of gas evolved from their own charge of coal. Prior to use, the gas is thoroughly cleaned and stripped of certain by-products by a series of cooling and scrubbing operations. The by-products usually recovered are gas, tar, ammonia, and light oil. Many secondary by-products are obtained from the light oil at separate plants. The pollution problems from the production of these secondary products are a considerably different problem and usually of only minor concern.

The crude gas, e.g., volatile products leaving the ovens is composed of the permanent gases whose mixture constitute the clean coke oven gas, in addition to gases or vapors of water, tar, ammonia, phenol, hydrogen sulfide, hydrogen cyanide, light oil, and naphthalene. Typical production rates of some of these materials are shown in Table 1. Many of these materials must be removed from the coke oven gas prior to use in order to prevent excessive plugging and corrosion of the distribution system. It is these gas cleaning and by-product recovery systems that produce the contaminated waste water.

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TABLE 1

TYPICAL QUANTITIES OF VOLATILE PRODUCTS PER TON OF COKE

Gas	15,000 ft.3
Tar	10 gal.
Light Oil	4 gal.
Ammonia	7 lbs.
Phenolics	0.6 lbs.
Hydrogen Sulfide	8 lbs.
Naphthalene	1.5 lbs.

The gas cleaning and by-products recovery system most widely used in the United States is the semidirect system. There have been a number of other systems proposed, some of which have been tried, and at least one of which, the indirect recovery system, is in full-scale operation. The principal differences between these alternate systems is the method of ammonia removal and the type of by-product ammonia recovered; i.e., ammonium sulfate, diammonium phosphate, or ammonium hydroxide. Figure 1 is a flow diagram of the semidirect system.

In the semidirect system the crude gas leaves the ovens through standpipes at the top, which connect to a large collecting main traversing the full length of the battery. The gas receives its first cooling in the collector main by contact with sprays of ammoniacal liquor which was previously condensed from the gas. This initial cooling results in the removal of approximately 85 percent of the tar. The gas then passes through the primary cooler where the remaining 15 percent of the tar is removed. The primary cooler may be the direct or indirect type.

From the primary cooler, the gas passes through the car extractor, an electrostatic precipitator, for removal of the last traces of tar. Condensate drains are provided at each piece of equipment from the collector main through the tar extractor. The condensate is sent to decanter tanks for separation of the tar. The recovered tar is used as fuel in the steel plant or sold to local chemical companies for the manufacture of a variety of secondary by-products. The tar-free liquor is pumped back to the collector main. Excess ammoniacal liquor resulting from condensation of gas moisture is sent to an ammonia still.

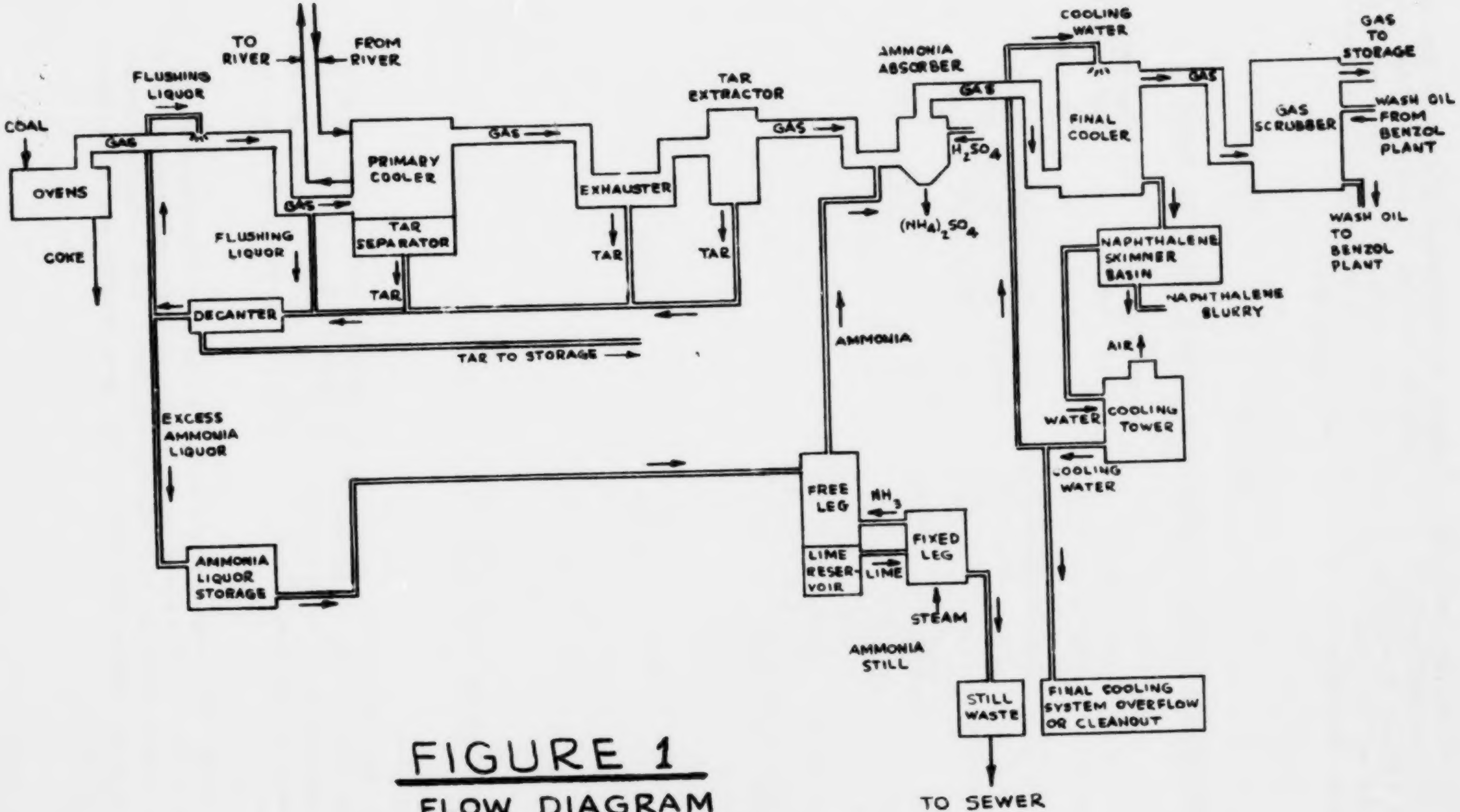
COAL
OVENS
COKE
GAS
FLUSHING LIQUOR
TO RIVER
FROM RIVER
GAS
PRIMARY COOLER
TAR SEPARATOR
FLUSHING LIQUOR
TAR
DECANTER
TAR TO STORAGE
GAS
EXHAUSTER
TAR
TAR EXTRACTOR
TAR
GAS
AMMONIA ABSORBER
H_2SO_4
$(NH_4)_2SO_4$
AMMONIA
GAS
COOLING WATER
FINAL COOLER
GAS
GAS SCRUBBER
GAS TO STORAGE
WASH OIL FROM BENZOL PLANT
WASH OIL TO BENZOL PLANT
NAPHTHALENE SKIMMER BASIN
NAPHTHALENE SLURRY
AIR
WATER
COOLING TOWER
COOLING WATER
EXCESS AMMONIA LIQUOR
AMMONIA LIQUOR STORAGE
FREE LEG
NH_3
LIME RESERVOIR
LIME
FIXED LEG
STEAM
AMMONIA STILL
STILL WASTE
TO SEWER
FINAL COOLING SYSTEM OVERFLOW OR CLEANOUT

FIGURE 1

FLOW DIAGRAM

SEMIDIRECT BY-PRODUCT COKE PLANT

The volume of excess ammoniacal liquor is dependent upon coal moisture content and varies from 30 to 35 gallons per ton of coke. This liquor contains (Table 2) a large percent of the total volatilized ammonia, nearly all of the phenol, and significant but unrecoverable quantities of cyanide, thiocyanate, sulfide, and chloride.

TABLE 2

TYPICAL ANALYSIS OF AMMONIACAL LIQUOR AND STILL WASTE

	Excess * Ammoniacal Liquor		Undephenolized (1) Still Waste		Dephenolized (1) Still Waste	
	Conc. (ppm)	Discharge lb./1000 tons coke	Conc. (ppm)	Discharge lb./1000 tons coke	Conc. (ppm)	Discharge lb./1000 tons coke
Ammonia	3800	1300	155	77	110	50
Phenol	1500	500	1320	725	158	71
Cyanide	20	7	-	-	-	-
Thiocyanide	600	200	-	-	-	-
Sulfide	2	1	-	-	-	-
Chloride	7000	2300	4350	2393	5400	2930
Volume						
(gal./ton coke)	33		55		45	

* Based on analysis from Armco Steel Corporation's Houston Coke Plant

Ammonia in the excess liquor is volatilized by live steam injection in the ammonia still. The volatilized ammonia is reinjected into the gas stream following the tar extractor. The gas is then scrubbed with sulfuric acid in the saturator for removal of ammonia as ammonium sulfate.

The waste water from the ammonia still is either dephenolized and discharged to a receiving stream or disposed of without dephenolization usually by evaporation at the quench station. Two dephenolization processes are in common use today. The most modern and efficient system is the liquid extraction process where benzol or light oil is used to absorb the phenol. It is later removed from the absorbent by caustic extraction to form a sodium phenolate by-product. The other dephenolizing system is the vapor recirculation process where the phenol is vaporized with steam. The steam and phenol vapors are then contacted with caustic to form sodium phenolate. Although these processes are quite efficient, the waste water discharged to the receiving stream still contains excessive amounts of phenol, ammonia, and cyanide.

Complete elimination of the water waste from the ammonia still can be accomplished by evaporation at the coke quench station. Although this method is rather widely used, it is an undesirable approach because of problems with corrosion of the tower, quench car, and local buildings and equipment. These problems are a result of the chlorides in the still waste.

Following the saturator the gas is cooled in the final cooler in preparation for light oil removal. Light oil is scrubbed from the gas by a high boiling wash oil in the gas scrubber. The light oil is then distilled from the wash oil and the wash oil is recirculated. The light oil is refined in the benzol plant by distillation and fractionation into benzol, toluol, and xylol. The gas is then ready for distribution.

By-product ammonia recovery from coking operations was a profitable business in the early 1900's. Since that time, an economical process for the synthesis of anhydrous ammonia has been developed. The use of this process has resulted in the steadily decreasing value of ammonium sulfate as well as other ammonium compounds. Today, the cost to produce ammonium sulfate is higher than its market value and in many locations there is virtually no market. In general, by-product ammonia recovery in American coke plants is no longer considered a profitable venture. At best it is an expensive pollution abatement measure. For this reason, emphasis on efficient operation of by-product recovery equipment in many plants has been reduced resulting in significant increases in the discharge of ammonia, phenol, and other materials as listed in Table 2. In other plants, the ammonia recovery equipment has been completely abandoned resulting in the direct discharge of ammoniacal liquor, and the required conversion of the final cooler to a once-through system.

The high cost of by-product ammonia recovery, as well as other available treatment and disposal systems and the inability of these systems to produce acceptable effluent quality at many locations, has resulted in the need for alternative pollution control methods. It is the purpose of this study to evaluate one such alternative--biological treatment.

SECTION IV

POTENTIAL SOLUTIONS TO PROBLEM

Many mechanisms have been considered to eliminate or reduce the amounts of ammoniacal liquor and for its treatment or disposal. This section will briefly describe some of the treatment or disposal methods other than microbiological that have been considered. Biological methods will be reviewed in the succeeding sections.

MODIFIED METHOD OF COKE PRODUCTION

Ammonia liquor itself is an outgrowth of changing technology in the manufacture of coke. At one time, the major source of coke in this country was from beehive ovens. These devices manufactured coke but no by-products and used the evolved gases to heat the oven by burning the gas within the oven itself. Thus, at no time was the gas allowed to cool and formation of ammoniacal liquor was avoided. However, because of air pollution problems and the desire to recover by-products and the gas itself, these units were replaced by the currently used slot-type ovens with the ammoniacal liquor problem. Currently, operational changes are being proposed which may reduce the amount of ammoniacal liquor produced and new coking techniques are proposed which may eliminate the problem.

One change which may reduce the quantity of ammonia liquor is to predry the coal prior to charging. This is a part of a new system being developed for smokeless charging of slot ovens. If the vapors evolved during predrying are not heavily contaminated and do not present a problem of disposal in themselves, then this would obviously reduce the quantity of waste. In addition, this might effect the amounts of other constituents, especially ammonia. Ammonia is known to be protected from thermal cracking by the presence of such oxygenated compounds as water. In fact, at one time, when ammonia was a valuable by-product of coking, steaming was considered as a method to enhance the yield. Conversely, it might be anticipated that less coal moisture would lead to reduced amounts of ammonia.

For several years, the coking industry has been seeking new methods for making coke. Currently, several continuous coking processes (2) are under development. The major attributes of these processes, according to their developers, is that they can coke coals that cannot be processed in the current slot-type ovens and that they reduce air contamination. No information on potential water pollutants is known; and until definitive information is available, the presumption must be made that problems equal to those in slot-type ovens will exist. However, it can be hoped that continuous coking of predryed coal may lead to a lower potential for water pollution.

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QUENCHING

After the coal has been carbonized, the hot coke is removed from the oven and is cooled by direct water sprays. This process is called quenching. Coke quenching as presently practiced uses about 500 gallons of water per ton of coke quenched with a loss of about 150 gallons per ton through evaporation. Some coke plants have utilized this evaporative loss to dispose of ammoniacal liquors as well as other wastes.(1, 3)

A major problem with the use of highly saline waste, such as ammoniacal liquor for quenching is the increased rate of equipment corrosion. The costs incurred from this corrosion are generally high and must be considered as part of the costs of disposing of ammoniacal liquor.

The concept of coke quenching as a method for the disposal of ammoniacal liquor was based on the supposition that the potential contaminating constituents of both air and water were burned by the heat from the coke. Unfortunately, however, instead of being destroyed, the volatile constituents are simply distilled and discharged to the atmosphere. This has been proven in the case of phenolics in one quenching operation (4) and while not as definitive, some information is available which indicates that sizeable amounts of the ammonia in the quench water is also released to the atmosphere.(5) The fate of these materials after release is not known. In certain instances, this process has been suspected of contributing to air pollution.

INCINERATION

Incineration has been considered as an optimum disposal method for many kinds of waste products including concentrated liquid wastes. For aqueous wastes, in general, the major economic consideration is the difference between the energy requirements for evaporation of the water and the energy recovered by combustion of the waste constituents. In the case of ammoniacal liquors, an additional problem is encountered. That is one of equipment corrosion resulting from the high inorganic chemical content (especially chlorides) of the waste. No doubt, incineration of this waste is technologically possible, but in light of the decreasing availability and the resultant increasing cost of fossil fuel, the desirability and the economic feasibility is seriously questioned. Rudolfs (6) reports that one installation in Germany evaporates and burns the residue. All of the waste water is evaporated directly into the air by gas-heated furnaces and most of the phenols were burned in the 250-foot furnace stack. Increased equipment corrosion is said to result.

DISTILLATION

The major conceptual difference between simple evaporation and distillation is that in distillation the vapors are recondensed while in evaporation the vapors are usually discharged directly to the atmosphere.

The equipment is generally much more complex for distillation than for evaporation but distillation lends itself better to both thermal and by-product recovery. Distillation, as a method for treating coke plant wastes, is not new and is currently the method of choice at many plants for removal of ammonia and phenolics from ammoniacal liquors. These specific processes will be covered later in this section.

One proposed process (7) is stated to treat completely a conventionally free ammonia distilled and dephenolized liquor by a modified distillation process. The liquor is distilled to a dry powder after addition of acid to retain the ammonia and activated carbon to retain the phenolics in the residue. The process appears to be fairly complex and no actual applications of the process are known.

DEEP WELL DISPOSAL

The use of deep injection wells for the disposal of wastewaters has grown rapidly in recent years. The advantages of this method of disposal as delineated by its proponents include: (1) complete disposal of waste; (2) minimum pretreatment needed; (3) no complicated equipment required; and (4) low operating cost. For coke plants located in a suitable injection area, disposal of ammonia liquor to a deep well is possible. Care would be required in the pretreatment step to assure the complete removal of tars and other suspended materials that might clog the aquifer. The compatibility of waste with the aquifer also needs to be carefully evaluated because of the many potential reacting chemical species involved. Two wells are known to be in operation for disposal of ammoniacal liquor. One of these wells is operated by Ford Motor Company in Detroit, Michigan, and the other is operated by Bethlehem Steel in Indiana.

Currently the use of injection is being reviewed from both a technological and legal framework and the future use of this process is being seriously questioned.

REMOVAL OR RECOVERY OF SPECIFIC CONTAMINATES

Most wastes are treated by methods which selectively remove specific contaminating substances which prepares the waste adequately for disposal, reuse, or further treatment. The contaminates of major concern in coke plant wastes are divided into two major categories: e.g., carbonaceous and nitrogenous compounds. The carbonaceous constituents of major concern have been phenolic in nature and much of the work has been directed toward the removal of this group of compounds. However, in certain instances, the removal of a broader variety of carbonaceous constituents is necessary and more general methods have been developed. The Nitrogenous constituent of major concern has been ammonia. The discharge of excessive amounts of ammonia to receiving waters can interfere with established beneficial uses for that water. Among the problems that have on occasion been attributed to ammonia are fish kills, stimulation of algae growth, interference with water disinfection, receiving stream oxygen deficiencies, and corrosion of copper pipes. Several somewhat specific methods of treatment have been developed for these constituents and the major ones of these will be reviewed briefly in the succeeding paragraphs.

Dephenolization

Dephenolization (1) or removal of phenolics from ammonia liquor for recovery purposes is widely practiced in this country. The two major methods in use are liquid extraction and vapor phase recirculation. In liquid extraction, a solvent is used to extract the phenolics from the ammoniacal liquor prior to ammonia distillation. A substantial part of the phenol is removed from the solvent by distillation or by extraction with strong caustic soda. The latter is preferred in this country. In the vapor recirculation process, water vapor is recirculated upward through a tower having two or three sections in series. The vapor first passes through one or two caustic soda scrubbing sections where it is freed of phenols, then on up the tower through the hot ammoniacal liquor from the free leg of the ammonia still. The vapor removes most of the phenols that remain in the liquor, then passes through a duct and blower to reenter the caustic soda section of the cycle. Neither system can be expected to remove more than 95-98 percent of the phenolics. The resulting dephenolized liquor may not be suitable for discharge in all instances.

Chemical Oxidation of Phenol

An excellent report (8) on the results of laboratory and pilot plant experiments has been prepared for the Ohio River Valley Water Sanitation Commission. This study on the oxidation of dephenolized ammoniacal liquors used chlorine, ozone, and chlorine dioxide. The wastewater treated contained from 30 to 300 mg/l phenolics, 300 to 400 mg/l of 5-day biochemical oxygen demand, and oxygen consumed (dichromate method) values of 1400 to 1800 mg/l. Removals of 60 percent of the BOD and OC were reported. Data shows that any of the oxidants tested could be used to remove phenolics. Approximately the following amounts of oxidant were required per mg/l of phenol to remove 90 percent of the phenolics when starting at levels above 100 mg/l: 30 mg/l for chlorine; 10 mg/l for chlorine dioxide; and, 4 mg/l for ozone. The major problem with chlorine was the apparent necessity to satisfy the ammonia demand prior to any oxidation of phenol.

Absorption of Organics

The removal of organic constituents in ammoniacal liquors by absorption on activated carbon was used in Germany in 1930.(9) In this plant, clarified carbonization wastewaters (coke filtered) was passed through beds of activated carbon. Effluent phenol concentrations down to 50 mg/l were reported. Other organics were also removed. When the activated carbon had taken up 6 to 10 percent by weight of phenolics, it was washed with benzene to remove phenolics and regenerated with steam. The phenolics were recovered by distilling the benzene. This plant apparently did not operate very long because of a drop in the price of phenol. A possible problem given in the cited reference concerns reactivation difficulties resulting from high boiling acidic and tarry constituents. Blackburn (10) and Ackeroyd (11) refer to operational plants using activated carbon in England. Regeneration is again with benzene and problems with tars have been reported. The Pittsburgh Coke and Chemical Company is reported (1) to have conducted a series of tests prior to 1950 using activated carbon but problems with regeneration were experienced.

Currently a renewed interest has been shown in the use of activated carbon to remove phenolics and other organics from ammoniacal liquors. The Calgon Corporation of Pittsburgh, Pennsylvania, has been testing and proposing a system including preclarification, absorption on a moving-bed of activated carbon, and thermal regeneration of the carbon. Several companies are considering this system but none is operational.

By-Product Production of Ammoniacal Compounds

The free ammonia in coke gas and the free and fixed ammonium compounds in ammoniacal liquor are frequently recovered, usually by the semidirect process as ammonium sulfate by bubbling the gas through a dilute sulfuric acid solution in the saturator. The crystals of ammonium sulfate are separated from the acid solution by means of a large basket centrifuge and are sometimes further dried in rotary dryers.(2) This process is widely used in the United States; however, the value of the sulfate has decreased in recent years to the point where it is no longer economical.

Theoretically, nitric acid would be an excellent absorbent for the recovery of ammonia from by-product gases, and the resulting ammonium nitrate would be a valuable material for both the fertilizer and explosive industries. Here again, however, the recovery cost exceeds market value of the by-product.

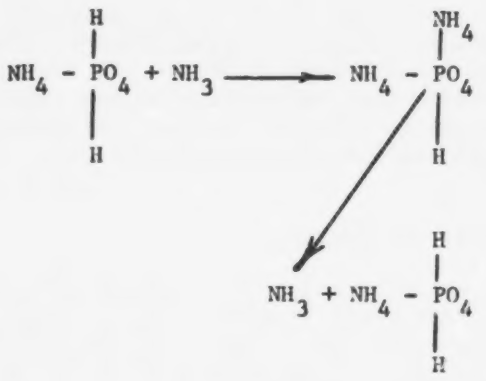
Ammonium thiocyanate has been produced from coke-oven gas by scrubbing the hydrogen cyanide in the gas with ammonium polysulfide solution.

$$NH_3 + HCN + S = NH_4SCN$$

In this process only the ammonia equivalent to the hydrogen cyanide content is removed. This amounts to about 20 percent of the total ammonia in the gas.

It would be ideal if economical methods were found whereby ammonia could be removed from coke-oven gas and subsequently recovered from the absorption system to yield a concentrated stream of gaseous ammonia which could then be condensed to anhydrous ammonia or processed further to any desirable ammonia chemical or derivative. At present, ammonia is being removed from by-product gases by three methods: (1) by absorption in sulfuric acid to produce ammonium sulfate; (2) by absorption in phosphoric acid to produce mono- or diammonium phosphate; and (3) in liquor plants by absorption in water to yield a dilute ammonia solution from which the ammonia is steam-stripped and reabsorbed to yield a concentrated 30% ammonium hydroxide solution sold as B liquor.(12)

The most promising of these chemical processes is the ammonium phosphate system. This method involves the absorption of ammonia in an aqueous solution of monoammonium phosphate which produces a solution of diammonium phosphate. The solution is subsequently regenerated by heating, which strips the ammonia, and restores the monoammonium phosphate solution.



Two processes have been proposed which involve absorption of ammonia to form ammonium sulfate and subsequent decomposition of the ammonium sulfate to yield a concentrated ammonia gas stream. One of the processes involves the decomposition of ammonium sulfate in the presence of zinc oxide in a moving bed system. In the upper part of the reactor ammonium sulfate is decomposed at 500°C to form zinc sulfate and ammonia according to the following overall reaction

$$(NH_4)_2SO_4 + ZnO \longrightarrow ZnSO_4 + 2NH_3 + H_2O$$

In the lower section of the moving bed reactor, the zinc sulfate is decomposed at 850-1000°C according to the following reaction

$$ZnSO_4 \longrightarrow ZnO + SO_3$$

The SO_3 is converted to sulfuric acid which is used to absorb more ammonia and the ZnO is recycled with fresh ammonium sulfate.

The second process developed by Inland Steel involves the absorption of ammonia in ammonium bisulfate solution according to the following reaction

$$NH_3 + NH_4HSO_4 \longrightarrow (NH_4)_2SO_4$$

The dried ammonium sulfate crystals are fed to a decomposition chamber heated to 650°F in which the fused ammonium sulfate is decomposed to gaseous ammonia and molten ammonium bisulfate according to the following reaction

$$(NH_4)_2SO_4 \longrightarrow NH_3(g) + NH_4HSO_4$$

The resulting ammonium bisulfate is recycled. The ammonia gas can be converted to anhydrous ammonia gas or absorbed in water to produce an aqueous ammonia. This process, while interesting, raises certain questions. Molten ammonium bisulfate was found to be extremely corrosive to a wide variety of metals.

Incineration of Ammonia

The Koppers Company has proposed a system for destroying ammonia in which the ammonia is absorbed from the coke-oven gas by water-scrubbing. The weak liquor is stripped with steam to obtain a concentrated stream of gaseous ammonia which is burned destructively.(12) Also described in a U.S. Patent (13) is a process of burning the stripping ammonia in a regenerator (part of the coke oven) at about 1200°C. Private correspondence (14) containing a report by R. E. Muder entitled, "Oxides of Nitrogen from Burning of Ammonia" presents his analysis of the proposal to dispose of coke plant ammonia by combustion. He concludes that burning of ammonia will not contribute any greater concentration of NO to the atmosphere than will normal gas combustion.

A brief study of the thermodynamics of the formation of nitric oxide during the combustion of ammonia has been made.(15) Thermodynamic data were obtained from U.S. Bureau of Mines Bulletin 605 (1963). The stable compounds formed during the combustion of ammonia are nitrogen and water. The only oxide of nitrogen that may be formed in small amounts is NO. Since nitrogen and oxygen are present during any combustion involving air, there is no thermodynamic reason why more nitric oxide should form when burning ammonia than when burning any other compound in air at the same temperature. If nitric oxide is formed in objectionable amounts, it could only be due to kinetic reasons. NO might be formed as an intermediate during the combustion of ammonia and might not be given a chance to reach equilibrium, which is unlikely. The equilibrium amount of NO formed increases with increasing temperature. Hence a cooler flame will minimize the formation of NO. A U.S. Patent granted to Rosenblatt and Cohn (16) deals with the combustion of ammonia

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

The reaction is accelerated at temperatures greater than 500°C using a precious metal catalyst.

Catalytic Decomposition of Ammonia

There is good reason to believe that techniques could be developed to destroy the ammonia by catalytic decomposition either in the coke oven or in the by-product stream.

The literature on the behavior of ammonia, its synthesis and decomposition is extensive. Recent reports by Samples, McMichael, Vigani and Arthur D. Little, Inc., give numerous references and an extensive review of the subject.(12, 17, 18, 19)

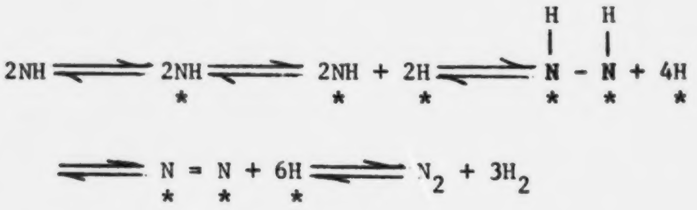
Ammonia is not a heat stable compound and at high temperatures will dissociate into its elements, hydrogen and nitrogen, according to the equation

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

The rate of decomposition can be increased with certain catalysts. A number of catalysts exist. The most common catalysts are iron oxides.

Considerable insight into the mechanism can be obtained by comparison between heterogeneous and homogeneous reactions with regard to the respective energies of activation. The activation energy for ammonia decomposition on a tungsten surface is about 41 kcal at 1043°C and more than 80 kcal without a catalyst at a temperature of 1200°C.(10)

The primary mechanism of ammonia decomposition on iron oxide can be shown as a two-step process: (1) chemisorption of ammonia on the iron catalyst to form iron nitrides and liberation of hydrogen, and (2) the subsequent desorption of nitrogen from the catalytic surface. From studies (20, 21) it is proposed that the rate-determining step for the decomposition reaction is the desorption of nitrogen.



$$2NH \rightleftharpoons \underset{*}{2NH} \rightleftharpoons \underset{*}{2NH} + \underset{*}{2H} \rightleftharpoons \underset{*}{\overset{\overset{H}{|}}{N}} - \underset{*}{\overset{\overset{H}{|}}{N}} + \underset{*}{4H}$$

$$\rightleftharpoons \underset{*}{N} = \underset{*}{N} + \underset{*}{6H} \rightleftharpoons N_2 + 3H_2$$

*represents a single absorption sight.

White and Melville (22) did some laboratory tests at the University of Michigan on the thermal decomposition of ammonia in the presence of other gases. This early work was done without the intentional addition of any catalytic agent and consequently, serves as a basis from which to start other studies. At 685°C with the following flow rates in cm^3/min, $H_2O = 4.0$, $CO = 22.6$, $NH_3 = 90.4$ the ammonia decomposition was 27 percent. From the geometry of the system, the estimated retention time in the heater at 100 cm^3/min is about 11 seconds. Other of their tests show that at one atmosphere of pressure, pure ammonia, ammonia with hydrogen, and ammonia with nitrogen decompose at the same rates. Some test runs using a porcelain tube instead of glass resulted in a 50-fold increase in percentage decomposition.

Charles L. Thomas in his new book "Catalytic Processes and Proven Catalyst" (23) discusses the ammonia decomposition reactions as follows - "This reaction may not ordinarily be thought of as a dehydrogenation but it has all the characteristics. It is used to generate small quantities of reducing gas, e.g., for metallurgical use. Catalysts of the type used for steam reforming of natural gas, i.e., Ni on refractory supports or iron oxide on similar supports, are used."

It would be ideal if means could be found whereby 95% or more of the ammonia could be destroyed even before it left the oven. A British Patent (24) claims the destruction of ammonia during the coking operation by the addition of iron oxide in water suspension to the upper stratum of coal in the coke oven. Up to 95% destruction of the ammonia is shown in the data presented in the patent, which provides the strongest support for this method of destruction which has been encountered.

Hill (25) has reported some related studies in regard to ammonia decomposition and coke ovens. It must be remembered that these investigations were carried out with the aim of increasing ammonia yield. He reports that Foxwell in 1922 found that iron (particularly in its metallic form in coke oven walls and in coke) was very detrimental as was lime. This effect of the surface material has previously been noted by White and Melville (in 1905), who found that fifty times as much decomposition occurred on rough porcelain as on smooth glass; and by Woltereck (in 1908) who observed that association started at 320°C in contact with metallic iron cloth, and at 420°C on oxide of iron. Heckel (in 1913) had observed the deleterious action of iron in practical oven tests. When coal to which blast furnace dust had been added was coked, the yield of ammonia decreased tremendously. Many other investigations were cited (19) but the conclusions are the same.

Wilson and Wells (26) state that the temperature of formation of ammonia is not the same for all coals. For some, ammonia formation begins at temperatures as low as 300°C, but with others temperatures in the range of 400 to 500°C are necessary. They add that in high-temperature coking, "the major portion of the ammonia is probably formed at temperatures above 600°C." Under favorable catalytic conditions this temperature should be high enough to decompose ammonia. This argument could be used to explain the ineffectiveness of attempts to decompose ammonia with flue dust. The information on the effectiveness in destroying ammonia by the addition of iron fines to the coal charge is contradictory.(12) Near complete destruction (95%) was obtained when the top of the coal charge in the oven was covered with a layer of iron oxide. However, the addition of flue dust to the coal mixture for ferrocoke resulted in only partial (20-40%) destruction of ammonia.

If complete destruction of ammonia can be achieved without affecting the quality of the coke, there will be no need for any ammonia removal equipment. This incentive justifies further experimental study to see whether essentially complete destruction in the oven is possible.(12)

Coke-oven gas after tar removal could be passed through a catalyst bed that would selectively decompose ammonia. The extent and rate of catalytic cracking on iron oxide catalysts increase with higher temperatures and become significant above 500°C and at temperatures around 700°C the dissociation is complete. At these temperatures, some of the higher organics in the coke-oven gas would crack, but the major components from the standpoint of heating value, methane and hydrogen would be stable. Also, the remaining important by-product, benzene should be quite stable at these temperatures, especially in the hydrogen-rich coke-oven gas atmosphere. The less important by-products toluene, xylene and naphthalene, would be progressively less stable at these high temperatures.

For the catalytic cracking of ammonia in the gas stream, four possibilities have been considered: 1) a fluidized bed with iron as bed material, 2) a moving pebble bed reactor using pebbles of iron or iron oxide pellets, 3) a pebble bed reactor consisting of two stationary beds of pebbles that are placed on stream and then regenerated periodically and 4) a thicker brick furnace consisting of two units with one on stream while the other is being regenerated by burning off deposits on the iron oxide bricks.

The fluid-bed system has the advantage of good gas-solids contact, accurate temperature control, and simplicity in handling of the catalyst. However, it suffers from higher pressure drop. The moving bed system is much too cumbersome and expensive. The fixed pebble-bed unit has the advantage of lower pressure drop and simplicity, particularly if the iron catalyst has long life. The most promising system appears to be the one involving parallel-fixed pebble units, using relatively cheap iron ore as the catalyst. The catalyst would either be regenerated in place intermittently by controlled oxidation with steam and air, or simply discharged. To accurately determine cost factors experimental work is necessary to study operating temperatures, gas velocity in bed, frequency of catalyst fouling, effect on light oil recovery and effect on the volume and heating value of the final coke-oven gas.

Ion Exchange for Ammonia

Ammonia exists in solution predominantly as the ammonium $(NH_4)^+$ ion unless the pH is higher than about 9.5. The ammonium ion is very similar to the potassium ion in size and is precipitated by the same reagents that precipitate potassium. Absorption of ammonium ion on ion exchange resins is ordinarily very similar to the absorption of potassium and sodium ions. Therefore, conventional water softening ion exchange resins which are selective for calcium and magnesium do a relatively poor job of removing ammonium from dilute solutions. Total deionization by mixed bed ion exchange resins will remove ammonium ions along with other cations but this process is too costly for wastewater treatment.(27)

Certain zeolites show unusual selectivity for the ammonium ion. A number of these have been investigated by the Atomic Energy Commission because they also show selectivity for cesium and potassium ions. A demonstration project at the Battelle Memorial Institute, Pacific Northwest (Hanford Laboratories) showed that certain zeolites including the naturally occurring mineral clinoptilolite had a high selectivity for ammonium in natural and wastewaters.

The process employs the natural zeolite which is selective for ammonium ions in the presence of sodium, magnesium and calcium ions. Regeneration of the exhausted clinoptilolite is accomplished with solutions or slurries containing lime. Lime provides hydroxyl ions which react with ammonium ions to yield an alkaline aqueous solution. This ammonia solution is processed through an air stripping tower to remove the ammonia. The problems of ammonia dispersion to the atmosphere are similar to those encountered in direct air stripping of ammonia. The spent regenerant is then fortified with more lime and recycled to the zeolite bed to remove more ammonia.

A cubic foot of granular clinoptilolite, regenerated with lime, was found capable of removing ammonia from more than 2000 gallons of secondary effluent. Ammonia removals exceeding 99 percent were obtained for two clinoptilolite columns in series during laboratory studies.(28)

In a private communication (29) with the Davison Chemical Division, Baltimore, Maryland, it was stated that they manufactured several forms of molecular sieves which are selective for ammonium ions when used as ion exchangers. They further state that there is evidence that thermal regeneration of these molecular sieves will produce nitrogen and water in a catalytic decomposition rather than simply releasing ammonia. This possibility should be investigated. Thermal regeneration occurs at about 550°C.

Air Stripping of Ammonia

Ammonia stripping is a modification of the aeration process used for the removal of gases from water. Ammonium ions in wastewater exist in equilibrium with ammonia and hydrogen ions as shown by:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O$$

As the pH of the wastewater is increased above 7, the equilibrium is displaced to the right. At a pH above 10 more than 85% of the ammonia present may be liberated as a gas by agitating the wastewater in the presence of air. This is generally done in a packed tray tower equipped with an air blower.(30)

Early studies of feasibility of stripping of ammonia from wastewater (Kuhn, 1956) showed a major difficulty: the volume of air per unit volume of water is very high, about 400 cubic feet per gallon of water in a countercurrent-flow packed tower.(31) Ammonia solubility is higher in cold water than in warm water, consequently, more air is required to remove it. For example, at 0°C it would take about 800 cubic feet of air per gallon of water to remove 90 percent of the ammonia.

There is also a question concerning the magnitude of the air pollution problem created by the ammonia stripping of ammonia liquors. In a study made at Mellon Institute (32) on stripping ammonia from hot excess liquors, concentrations as high as 6000 mg NH_3 per cubic meter of air were obtained. It is unlikely that this concentration of ammonia could be discharged to the atmosphere.

Reverse Osmosis for Ammonia

Reverse Osmosis (33, 34) involves the forced passage of water through membranes often cellulose acetate, against the natural osmotic pressure. The wastewater must be subjected to pressures up to 750 psi to accomplish separation of water and ions.

Proposed mechanisms for the action of the cellulose acetate membranes used in reversed osmosis cells include sieving, surface tension, and hydrogen bonding. Although plausible, the sieving theory does not explain the action of the membrane in removing small ions. For example, sodium and chloride ions, which are approximately the same size as water molecules would easily pass through the membrane.

Problems associated with the application of the reverse osmosis process include concentration polarization, membrane fouling, the passage of certain ions through the membrane, and disposal of the concentrated waste fraction. In a recent study of the use of this process for the removal of nitrates from irrigation return water, it was found that a portion of the nitrate ions passes through the membrane, thereby limiting its usefulness in this application.

Chemical Oxidation or Reduction

The chemistry of aqueous nitrogen compounds is complex and the number of possible oxidation or reduction reactions is great. Since nitrogen gas represents an intermediate redox state for nitrogen and a much desired end-product for nitrogenous removal, much effort has been devoted to seeking applicable reactions. Most of these efforts have been specifically aimed at the relatively low concentrations of nitrogenous materials found in sanitary sewage but in principle the results apply to ammoniacal liquors as well. Two sets of reactions are possible, oxidation of ammonia or reduction of nitrate or nitrite to nitrogen gas. The best known reaction for the production of gaseous products from the oxidation of ammonia is the breakpoint reaction with chlorine. This reaction requires more than 8 mg/l of chlorine for each mg/l of ammonia oxidized. The chlorination of ammoniacal liquors could utilize electrolytic production of chlorine because of the inherent high chloride concentration.

Chemical reduction of nitrates in dilute solution has been proposed by several investigators. Young, et al, (35) proposed the use of powdered iron as the reducing agent. Unfortunately, most of the nitrate is reduced to ammonia under the conditions specified. Gunderloy, et al, (36) made an extensive study of denitrification by chemical means and came to the conclusion that ferrous iron was the reductant of choice. Results indicate, however, that only about half of the nitrate reduced is lost; the remainder becomes ammonia. An excellent review of the oxidation and reduction reactions between inorganic nitrogenous constituents has been prepared by Chao and Kroontje.(37) In this review numerous potential pathways for the production of nitrogen gas from nitrogenous compounds are given. The complexity of the possible reaction schemes makes theoretical evaluation almost impossible and reliance on experimental information is a must. A possible pathway is described which involves ferrous iron reduction of oxidized forms of nitrogen. A laboratory evaluation of this technique was attempted and results are summarized in the Appendix.

SECTION V

BIOLOGICAL OXIDATION AND DENITRIFICATION

BIOLOGICAL OXIDATION OF COKE PLANT WASTES

The use of biological methods for the treatment of various waste waters from coke plants has been practiced for many years, especially in Europe. The earliest investigations were concerned with the treatability of still wastes in conjunction with municipal wastes specifically for the removal of phenolic compounds. According to Rudolfs,(38) who provides an excellent summary on the biological treatment of coke plant wastes to 1953, the initial efforts were made in the late 1800's. These early experiments concluded that with municipal wastes, with dilution factors of about 200, satisfactory removals of phenolics and thiocyanates were possible. During the ensuing seventy years, numerous efforts, many highly successful, have been made to treat a variety of ammoniacal liquors, using both trickling filters and activated sludge, with and without municipal sewage, and with and without dilution. Some of these efforts that have particular historical interest or have direct bearing on the design of the current experiment are outlined in the following paragraphs.

The first extensive investigations were reported in 1907 by Frankland and Silvester (39) who utilized bacterial contact beds and trickling filters to satisfactorily treat a mixture of 9 percent ammonia still waste in municipal sewage. A most interesting experiment was conducted by Fowler and Holton (40) when they successfully treated ammonia liquor using a trickling filter of crushed clinker. Essentially, this plant consisted of a trickling filter with a recirculation ratio of nine to one. This is the first reference to the treatment of ammonia liquor without the use of an external diluent. Even though these and other experiments were reported, Key (41) in 1935 concluded that when still waste does not constitute more than 0.5 percent of the influent of a municipal sewage treatment plant, no adverse effects on treatment will be noted.

The first reported recognition of the fact that ammonia liquors are deficient in phosphorous is credited by Rudolfs to Nolte in Germany in 1939. Nolte proposed an activated sludge process supplemented by available phosphates.

One of the very early efforts in the treatment of ammoniacal liquors in this country is recorded in a patent assigned in 1922 to the Koppers Company.(42) This study, both laboratory and pilot scale, showed that the phenolic content of properly diluted waste could be greatly reduced. The first use of activated sludge in the United States for the treatment of still wastes was by the Milwaukee (Wisconsin) Sewerage Commission

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according to Rudolfs (38). These experiments were conducted to determine if still waste could be treated in a municipal treatment plant. The results of this extensive investigation showed that phenolics were removed as determined by taste test when the mixture treated consisted of 2 percent still waste in municipal sewage. Additional experimental evidence indicated that the phenolic wastes could be treated at considerably higher concentrations and in some cases mixtures containing as high as 15 percent were treated satisfactorily.

A series of detailed laboratory and field experiments were conducted by the Chicago Sanitary District and reported by Mohlman (43, 44). The treatment criteria defined by these investigations included the limitation on phenolics of 30 to 40 ppm in the mixture to be treated. The effect of temperature on phenolic removal was also noted, removal being enhanced by increased temperatures.

Two cooperative investigations between the Gary (Indiana) Sewerage Commission and the United States Steel Company have been reported (45, 46) on the disposal of still wastes in an activated sludge process. In the earlier report with a minimum dilution factor of approximately 1 in 40 and an influent phenolics concentration of about 20 ppm, the plant effluent contained only a few ppb of phenolics. The latter reference includes the results of a new series of experiments conducted during 1966-67. During this period, a maximum still waste flow of almost 400,000 gallons per day was treated along with a flow of domestic sewage of about 40 mgd giving a treatment concentration of only one percent ammonia liquor. The approximate aeration time, as computed from data given in the paper, is nine hours. The removal of phenolics was essentially complete. A major obstacle to the discharge of ammonia liquor was the excessive chlorine demand of the plant effluent. In the paper, this was attributed to the more than 16,000 pounds of ammonia being contributed by the ammonia liquor. The municipal waste alone contributes approximately 5,000 pounds of ammonia. The conclusion that excessive ammonia concentrations were responsible for this chlorine demand is questioned on the basis that ammonia exerts a chlorine demand only when subjected to breakpoint chlorination. The detailed chemistry of breakpoint chlorination is beyond the scope of the present report but it can be shown that ammonia exerts no demand until chlorinated beyond a one-to-one molar ratio. On a weight basis this corresponds to a ratio of 5 chlorine to 1 ammonia-nitrogen. Thus, the ammonia in the municipal waste alone would not exert a demand until after over 60 mg/l of Cl_2 were added and with the combined waste, over 250 mg/l would be required. Since activated sludge plant effluents generally are disinfected by chlorine dosages of less than 10 mg/l, no chlorine demand resulting from ammonia would be expected either with or without ammonia liquor. The more obvious explanation for the chlorine demand and the resulting abandonment of the combined treatment program is unremoved thiocyanate contributed by the ammonia liquor along possibly with unreacted thiosulfate from the same source. No actual data on these constituents is reported. Approximately 85 percent of the cyanide was removed in the treatment plant.

The combined treatment of ammoniacal liquors and municipal wastes is practiced in the Chicago area. For example, Interlake Steel Corporation discharges about 60,000 gallons per day of still waste plus some other coke plant wastewaters and Wisconsin Steel Division of International Harvester Company discharges about 100,000 gallons per day of undistilled ammoniacal liquor plus other wastes to the Calumet System of the Metropolitan Sanitary District. This apparently successful treatment system operates at about a one percent liquor concentration. The East Chicago activated sludge system accepts about 150,000 gallons per day of lime distilled and dephenolized liquor from Inland Steel Corporation and 350,000 gallons per day of still waste from Youngstown Sheet and Tube Company. The concentration of liquor in this instance is over 5 percent but much of it has been dephenolized and lime distilled.

Several noteworthy attempts have been made to treat ammonia liquors without dilution with domestic wastes. A United States Steel report (47) outlines a series of experiments utilizing a large scale pilot-plant to determine the treatability of still wastes containing various concentrations of phenolics. The results indicate a strong influence of initial phenolic concentration on the required period of aeration for obtaining an effluent with less than one mg/l of phenolics. To obtain this effluent concentration required average aeration times of 9.4, 25, and 100 hours for initial phenolic concentrations of 10, 40, and 300 mg/1, respectively. No mention is made of sludge concentrations involved in the above tests but the results tend to indicate that they must have been low.

In 1957, Bethlehem Steel Corporation (48) began a pilot-plant study which has evolved into a full-scale treatment facility for ammoniacal liquor. The general conclusions drawn from the experimental phase of the project were that phenolic loadings of 30 pounds per day per 100 cubic feet of aeration capacity could be successfully treated with sludge concentrations of 5700 mg/l and a theoretical waste aeration time of 17.5 hours. Loading rates of this magnitude were not recommended, however, because of the difficulty in operating the system. At phenolic loading rates below about 12 pounds per day per 100 cubic feet and at sludge ratios below 0.7 pounds of phenol per day per pound of sludge the system is reported to operate smoothly. Probably the most controversial conclusion from this work has been with reference to the limiting concentration for ammonia in the system. Ammonia is reported to severly inhibit the biological sludge at concentrations of 4000 mg/l and the ammonia concentration is considered the "key design consideration for successful oxidation of weak ammonia liquor." Among other important treatment parameters found were tar, temperature, nutritional requirements, and pH. Recommendations included, limiting ammonia to 2000 mg/l in the biological reactor, removal of tar by storage of the liquor at ambient temperature, maintenance of reactor temperatures of 80-95°F, addition of phosphorus as phosphoric acid in a ratio of P to phenol of 1 to 70, and keeping the pH of the effluent between 6 and 8. The full-scale plant, designed on these results was put on stream in September of 1962. This plant consists of a storage tank, aeration tank, and clarifier, The storage tank receives the weak ammonia liquor directly from the coke plant and provides a detention time of approximately 9 days for equalization and tar removal. The waste after leaving the storage tank but prior to its introduction into the activated sludge aeration tank is diluted with water for control of ammonia concentrations to less than 2000 mg/l, is dosed with phosphoric acid to provide necessary phosphorus, and is steam heated. The aeration time, based on the undiluted discharge of weak ammonia liquor, is about 56 hours. Sludge separated in the clarifier is mostly returned to the aeration tank with excess sludge discharged to the municipal sewerage system. The design capacity of this plant is more than 4000 pounds of phenol per day; the average phenol load only 1300 pounds per day. At this loading of less than one-third of design capacity, the effluent phenol concentration, except during minor upsets, has remained below 0.1 mg/l. The efficiency of removal of biochemical oxygen demand (BOD-5) has been 85-95 percent. Removals of thiocyanate have ranged from 20 to 99 percent and averaged about 70 percent.

Several methods for improving the plant's capacity for thiocyanate oxidation and cyanide removal have been pilot-plant tested by Bethlehem Steel. These include the following: (1) a single-stage activated sludge system in which the effects of many variables were studies, (2) two activated sludge systems in series, (3) a slag trickling filter in series with an activated sludge system, and (4) a plastic-media trickling filter in series with the full-scale plant. Reportedly, only the treatment on the slag filter which oxidized up to 2.7 pounds per day of thiocyanate per 100 cubic feet and removed 50 to 65 percent of the cyanide was effective.

Just before the Bethlehem Steel Company's plant went on stream, Lone Star Steel Company (49) in Texas began operating a full-scale activated sludge plant on ammonia still waste liquor. The plant was designed to reduce influent concentrations of phenols of 100 to 800 mg/l to less than one mg/l for a waste flow of 50,000 gpd. The plant provides a pretreatment storage pond, an aeration time of about 24 hours, a heating unit to maintain temperatures above 70°F, a caustic feed pump to control pH in the range from 7 to 8, a phosphoric acid feeder, and provisions for sludge recycle. From the pilot-plant tests conducted to determine design criteria, it was established that treatment efficiency was not enhanced by aeration chamber oxygen concentrations exceeding 0.5 mg/l. In actual practice oxygen levels of 0.7 to 3.0 mg/l have been maintained and have proven to be satisfactory. A loading factor of 0.2 to 0.25 pounds of phenolics per day per pound of aerator suspended solids was found to give optimum results. The best range for suspended solids in this plant is 2500 to 3500 mg/l. In actual plant operation, influent phenolic concentrations of 250 to 475 mg/l and effluent concentrations of 0.1 to 0.3 mg/l have been experienced with partial removal of cyanides.

Dominion Foundries and Steel of Hamilton, Ontario, Canada have been operating a biological treatment plant processing ammoniacal liquor since 1968. This plant, as described by Ludberg and Nicks, (50) provides for tank storage of the waste for a period of about 2.5 days, prior to treatment, dilution of the waste to 50 percent strength to control ammonia, phosphoric acid addition, and aeration time based on undiluted waste of 37 hours, and a sludge recirculation rate equal to the flow of diluted waste. The dilution rate is provided to reduce and maintain reactor ammonia concentrations to less than 1200 mg/l. From average monthly data given in the paper, the plant has processed diluted waste concentrations of phenolics ranging from about 260 to 400 mg/l with effluent concentrations ranging from about 0.8 to 3.6 mg/l.

The removal of thiocyanate at the Dofasco plant has been erratic. According to the report, the principal difficulty is that strains of bacteria that most effectively oxidize thiocyanate function best at a pH lower than is present in the aeration tank. The optimum pH for these bacteria being about 7 with a range of 6.5-7.6. The actual aeration tank averages about 8.3. A longer retention time is also stated to be beneficial and a second set of aeration tanks operating in series with the present ones is suggested.

In addition to these actual plant operations, two recent laboratory investigations are worthy of note. One of these studies was conducted by the Koppers Company (51) to determine the treatment necessary to process crude ammonia liquor, free leg ammonia liquor, and ammonia still waste. The experiments were conducted in complete-mix activated sludge units providing an aeration period of 24 hours for a waste diluted to 25 percent for ammonia control. Results indicate that the three waste streams vary in treatability and that differing design criteria are needed for each.

International Hydronics Corporation (51) has investigated the use of several pretreatment steps for ammoniacal liquors to provide a more easily treated waste. Essentially, the processes proposed remove substantial amounts of the ammonia and cyanides prior to biological treatment by stripping, chemical precipitation, and coagulation. Process claims include amenability to biological treatment without dilution. A modified biological system called Bio-carb which is a mixture of activated sludge and activated carbon is also reported. This process produces an effluent low in carbonaceous materials and especially low in odor and color as compared with other biological processes.

The scope of this literature review on the biological oxidation of ammoniacal liquors has made no attempt to cover the vast numbers of references on the subject. For example, very little of the research and experience from either England or Germany has been included although much of this work is reflected in the experiments and operating results already described.

However, discussion on the subject of the biological treatment of coke plant wastes would be remiss without mention of the outstanding paper of Ashmore, et al (52) in 1967. This laboratory study on the application of the activated sludge process to the treatment of carbonization effluents without sewage was conducted with special emphases on the role of the sludge and the effect of effluent constituents on treatment. In these experiments, utilizing completely mixed activated sludge treatment units, the criterion for successful treatment was reduction of the 4-hour permanganate value by 90 to 95 percent accompanied by consistent removal of phenolics, thiocyanate, and thiosulfate to a few mg/l. These studies were conducted on either free or lime distilled liquors.

Among many interesting observations reported were the results of studies conducted to determine the limiting concentrations of various substances that could be tolerated by an operating system. Among the important limits found was one for chlorides. The conclusion reached was that ammonium chloride concentrations as chloride below 2000 mg/l had no effect but that larger concentrations were increasingly detrimental. Data is given which indicates that at ammonium chloride levels of 10,000 mg/l as chloride no more than 1000 mg/l of thiocyanate could be treated effectively and that this figure fell to 500 mg/l at a chloride concentration of 20,000 mg/l. This latter chloride concentration corresponds to about 8000 mg/l of ammonia-nitrogen. However, it was shown conclusively that the detrimental constituent was chloride rather than ammonia by substitution of sodium chloride for the ammonium chloride in subsequent experiments.

In the presence of phenolics, the chloride effect was found to be more important and for a given concentration of thiocyanate, the chloride which could be tolerated in the aeration vessel and still permit total thiocyanate removal, decreased with increasing phenol concentration. For example, whereas an influent containing 1000 mg/l of thiocyanate could be treated in the presence of 10,000 mg/l of chloride only 2500 mg/l of chloride could be tolerated when 1100 mg/l of phenolics were present in the influent. This synergistic effect makes extrapolation from one waste to another both difficult and uncertain.

Other interesting observations for the successful treatment of these wastes include operation in the endogenous respiration phase to assure high removals and levels of sludge wastage ranging to ten percent per day. Recommended ranges of aerator pH were 6.7 to 7.3. Cyanide above a concentration of about 40 mg/l was found to be inhibitory and when present along with sulfide was especially bad. The refractory organics present after treatment appear to be a most important but poorly understood parameter. This constituent is known to influence the dilution necessary for efficient treatment, is associated with the effluent color, and its detrimental effect is enhanced by heating and high pH. This latter point along with the fact that calcium thiocyanate is at about a factor of four more difficult to oxidize than ammonium thiocyanate may make lime-distillation a poor pretreatment procedure.

BIOLOGICAL NITRIFICATION AND DENITRIFICATION

No previous applications of the processes of nitrification and denitrification have intentionally been made to remove nitrogenous constituents from ammoniacal liquors. The use of these processes has been proposed to remove ammonia from municipal wastes and both are active mechanisms in the transformations of nitrogen in nature. The basic research on the two mechanisms has essentially all been conducted with regard to nitrogen in soil and its affects on agriculture. Many excellent reviews on these processes in these areas are available and include those of Delwiche,(53) Fry,(54) and Alexander.(55) The following paragraphs include a brief summary of the pertinent information from these sources.

Nitrification is the biological process of converting ammonia to nitrite and nitrate. In nature the two genera of bacteria responsible for these changes are Nitrosomonas for ammonia to nitrite and Nitrobacter for nitrite to nitrate. These organisms are strictly aerobic chemosynthetic autotrophs. This means that these organisms utilize oxygen to oxidize ammonia and nitrite to obtain energy to metabolize carbon dioxide into cellular materials. These organisms are truly remarkable when it is considered that they have the ability to synthesize from carbon dioxide, bicarbonate, or carbonate the vast array of polysaccharides, structural constituents, amino acids, vitamins, enzymes, etc., necessary for life. The simplicity of their nutritional requirements is of course accompanied by a tremendously complex metabolic system.

The capacity of these bacteria to utilize carbon dioxide or other inorganic carbonaceous materials depends on their ability to obtain energy from the oxidation of ammonia and nitrite for the purpose of reducing the inorganic carbon to organic carbon. Chemically these reductions may be represented as follows:

1) Ammonia oxidation (Nitrosomonas)

$$NH_4^+ + \frac{3}{2} O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad F = \text{ca.} - 60 \text{ kg. cal./mole}$$

2) Nitrite oxidation (Nitrobacter)

$$NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^- \qquad F = \text{ca.} - 20 \text{ kg. cal./mole}$$

3) Carbon dioxide reduction

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad F = \text{ca.} - 120 \text{ kg. cal./mole}$$

Using these equations, the approximate free energies, and experimental results on the amounts of carbon assimilated, the efficiency of energy transformation can be calculated. The ratios of carbon assimilated to nitrogen oxidized by Nitrosomonas has been found to vary from approximately 14 to 70:1 and for Nitrobacter 76 to 135:1. The organism efficiency is then 3 to 14 percent. A major fallacy in these computations may be the selection of water as the reducing agent in the conversion of carbon dioxide with the production of oxygen. Although this reaction is the primary one in photosynthesis it may not be the major one in this particular chemosynthetic process. Thus, the efficiency of the systems are questionable. However, the important parameter from a waste treatment point of view is not the energy requirement but the overall stoichiometry between the amounts of nitrogen oxidized to the amount of carbon reduced. If the above ratios of nitrogen to carbon are assumed to hold in waste treatment, then for every 1000 mg/l of ammonia-nitrogen oxidized, about 20 and 70 mg/l of organic carbon would be fixed. If this carbon is in the average oxidation state of zero, then this quantity would have a theoretical, chemical or biological oxygen demand of about 50 to 190 mg/l as O_2. Concurrently an oxidation resource of almost 3000 mg/l as O_2 has been formed as nitrate if subsequent denitrification to nitrogen gas is assumed.

Some interesting consequences of this fundamental research that effect the application of this process to waste treatment include bacterial growth characteristics as characterized by kinetics, pH requirements, and inhibitors. Early investigators found these organisms to be very slow reproducers. Isolation of pure cultures of the nitrifiers is difficult because this slow growth favors the more rapidly growing heterotrophs. A very similar problem occurs in waste treatment.

Nitrifiers are favored by pH levels above 6 and many of the species prefer a slightly alkaline medium. Since nitrification is accompanied by the release of hydrogen ions, unless adequately buffered the process can become self limiting due to a decrease in pH. These organisms are known to find limestone beneficial and tend to coat the mineral. Both the necessary buffering and the inorganic carbon requirement are satisfied by the limestone.

Denitrification occurs when facultative heterotrophic organisms utilize nitrate and nitrite as an oxygen substitute and produce nitrogen gas. In the field of agriculture, denitrification leads to a loss of available nitrogen which is disadvantageous; in waste treatment, the process is most desirable. While only a limited number of organisms are capable of oxidizing ammonia and nitrite, many are capable of reducing nitrite and nitrate. Two distinct reduction reactions are possible. One of these results in the formation of amino nitrogen which becomes a part of the cellular synthesis of the bacteria. The other, true denitrification, utilizes the two anions, nitrate and nitrite, as metabolic hydrogen acceptors. This latter mechanism allows certain organisms to grow anaerobically in media that would otherwise only support their growth in the presence of oxygen.

The metabolic pathways for nitrate reduction are not definitely known and it appears that pathways may be different for differing organisms. The major postulated reactions are given in Figure 2. The first step in reduction of nitrate involves its conversion to nitrite by an enzyme nitratase. Some organisms are capable of this reduction step only but others continue the reduction and many reaction pathways have been postulated. Certain organisms are capable of almost quantitative conversion of nitrite to ammonia, through the amino acid - protein route. Of the total nitrogen being chemically reduced during intensive denitrification as practiced in waste treatment, the fraction of nitrogen reduced through this mechanism will be small. The major reduction product of nitrite is hyponitrous acid. This compound is unstable and can be further reduced to yield ammonia or nitrogen gas either directly or through the intermediates nitrous oxide (N_2O) or hydroxylamine (NH_2OH). The pathways leading to nitrogen gas are, of course, to be favored for the denitrification of waste waters.

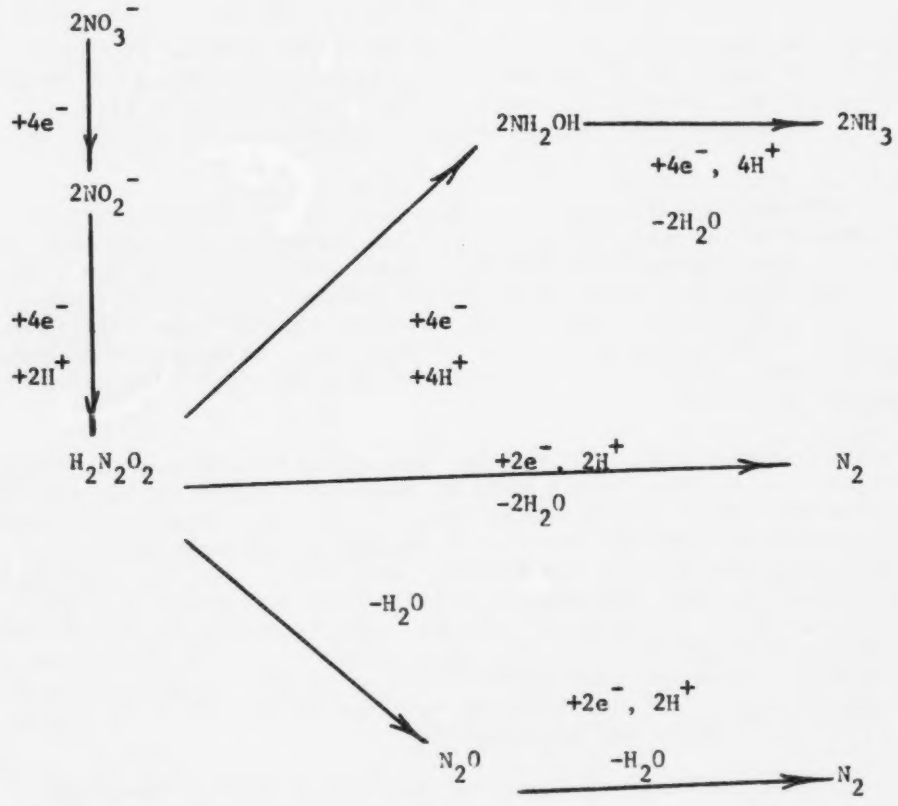

FIGURE 2

Hypothetical Pathways of Nitrate Reduction in Micro-organisms

In addition to indicating the postulated reaction products for denitrification, the figure shows the numbers of electrons, chemical ions, and molecules involved in the reduction. The electrons shown are all utilized in changing the nitrogen to a more reduced state. These electrons can only be derived from a chemical oxidation.

In denitrification, this normally is some form of organic material, the oxidation of which produces carbon dioxide. These organisms do not depend on the availability of nitrate or nitrite but utilize these materials only as a substitute for oxygen when it is unavailable. Thus, in the presence of both oxygen and nitrate, most potential denitrifiers grow aerobically with little or no effect on the nitrate; without oxygen they grow anaerobically utilizing nitrate as their electron acceptor. Most substances utilized for aerobic oxidation are utilized with equal facility in media containing nitrate. There are denitrifiers capable of utilizing sulfur, thiosulfate, and even hydrogen as replacements for organic carbon as energy sources.

The second major point of note is that two moles of hydrogen ion are utilized in the reduction of one mole of nitrate to nitrogen gas. Thus, denitrification will tend to increase the pH whereas nitrification lowered it. In denitrifying concentrated solutions, pH control may be necessary.

The major environmental influences on denitrification in nature are the type and amount of organic matter, oxygen concentration, acidity, and temperature. The influences on nitrate demand are essentially the same as those that affect the biochemical oxygen demand except for the oxygen concentration. In denitrification the important oxidants are nitrate and nitrite rather than oxygen as in BOD. In addition, the presence of oxygen inhibits denitrification by supplanting a portion or all of the demand of the organisms for a hydrogen acceptor.

The actual experience with nitrification and denitrification as a mechanism for nitrogen removal from waste waters is entirely related to its use for sanitary wastes. These wastes differ considerably from ammoniacal liquors from coke plants in that they contain on an average about 20 mg/l of ammonia-nitrogen. Coke plant wastes may contain more than 250 times this amount. Therefore, much care must be exercised in attempting to extrapolate from one waste to another. However, much excellent experience has been gained on this weaker waste and was the background for this phase of the project. Among the many papers found to be helpful were those of Ludzack and Ettinger,(56) Balakrishnan and Eckenfelder,(57, 58) Barth,(59) Downing,(60) and Downing and Hopwood.(61)

Downing was among the first to recognize and define some of the complex factors involved in maintaining nitrification in a conventional activated sludge system. The initial laboratory experiments with coke plant wastes quickly indicated that nitrification would be most difficult to obtain in a single-stage activated sludge unit also responsible for oxidation of the carbonaceous constituents. This difficulty results from several factors. The nitrifying sludge population is difficult to maintain in sufficient concentration in a single unit because of the necessity of wasting large amounts of sludge resulting from the removal of large amounts of organic contaminants. In addition, nitrification is known to be inhibited by high concentrations of organic materials and by relatively low levels of heavy metals and cyanogens. The obvious choice was to revert to separate carbonaceous and nitrification units in which sludges and sludge-wasting could be independently controlled. With the addition of the also independent denitrification unit, the plant for processing coke plant wastes for both carbonaceous and nitrogenous removals becomes a three-stage biological treatment operation. Barth (59) also has recommended the use of the three-sludge system.

The first unit of three-sludge system is for the removal of the bulk of the carbonaceous materials and is essentially the same as a normally operated activated sludge system. It consists of an aeration compartment, sedimentation compartment, capability for sludge recycle, and facilities for wasting of sludge. The second or nitrification stage then receives for its influent a waste low in carbonaceous matter and high in ammonia. This system physically is similar to the first stage which allows independent selection of operational variable to maximize nitrification efficiency. The third step, denitrification, as a result of its anaerobic nature, is necessarily separate and consists of a mixed reactor with reductant feed in addition to sedimentation and sludge recycle capabilities.

The reducing agent utilized in the denitrification stage must be carefully selected because it can have a large influence on both the ease or difficulty with which the unit operates and on the cost of operation. Finsen and Sampson (62) present an excellent review of several possible reducing agents and describe some of their experimental results. Among those discussed are various sugars, alcohols, molasses, and the residual reductants in treated sewage. The latter were not found to be in a form suitable to act as a hydrogen donor (reducing agent) in the process. Sucrose was tried at a ratio of 12 to 18 mg/l per mg/l of nitrate-nitrogen. The use of sucrose was abandoned because the effluent was very turbid and had a reminiscent of an alcoholic fermentation. Ethyl alcohol was also tried. The alcohol was dosed at 523 parts per million with good results. However, if it is assumed that the alcohol is oxidized to completion, this concentration theoretically should have been capable of reducing more than 380 parts per million of nitrate nitrogen. When decreases in alcohol dosage rates were attempted, the unit's behavior became erratic. Return of the unit to sucrose feed with careful adaptation proved that the unit could utilize sugar efficiently. However, the expense of sucrose or ethyl alcohol was considered prohibitive. A survey of alternative sources of hydrogen donors indicated that corn sugar molasses might be satisfactory.

A major difficulty with molasses was found in the storage and dosing of the material. Diluted molasses suitable for pumping quickly became contaminated with bacteria and fungi but addition of 10 percent sodium chloride to the diluted stock provided a solution to this problem. Among the conclusions of Finsen and Sampson concerning the use of molasses were that an excess of molasses amounting to about 20 mg/1 of chemical oxygen demand was necessary to get essentially complete denitrification. The ratio of molasses utilized as measured by COD as compared to nitrate reduced was about 50 mg/1 of COD to about 15 mg/1 of nitrate-nitrogen.

SECTION VI

DESCRIPTION OF PILOT PLANT

The pilot plant was designed to treat excess ammoniacal liquor at rates up to 1 gpm. It was built in modular fashion as shown in Figure 3. Three nearly identical modules were arranged in series so that each successive module would receive treated waste water from the preceding system. The first module was for oxidation of carbon compounds. The second and third modules were for oxidation of ammonia to nitrate and reduction of nitrate to nitrogen gas, respectively. Each of the modules were designed as individual and independent treatment systems. Other than the dependence of one module on another for a source of waste, the operating variables of each unit were independent of the others. Because of the toxicity of high concentrations of phenols, cyanides and other compounds in coke plant waste, each of the treatment systems was designed as a completely mixed activated sludge system. This design concept was utilized because it is much less sensitive to high influent concentrations and large variations in influent composition than other available systems.

Excess liquor from the coke plant tar decanters, flows by gravity to one of two storage tanks prior to treatment. These tanks are provided to reduce the liquor temperature from 150° F to 100° F or less, the optimum range for biological activity. In addition to temperature reduction, the storage tanks remove tar which escaped the decanters. It has been previously reported that the residual tar content of excess ammoniacal liquor inhibits biological activity.(48) Each of the storage tanks has a capacity of 1500 gallons or 24 hours at design capacity. The tanks are operated on a fill and draw basis. Alternately, one tank is cooled while the other is supplying waste for treatment.

The cool, tar-free liquor is pumped from the storage tank to the first treatment module for aerobic oxidation of carbon compounds. The first module consists of a completely mixed aeration tank and final clarifier. Equipment details are listed in Table 3.

The aeration tank is a cylindrical steel tank with a detention time of 24 hours at 1 gpm. It is equipped with a 3 horsepower submerged turbine mixer-aerator. Compressed air at up to 300 scfm is spurged under the turbine to provide oxygen for biological growth. Temperature control is provided by live steam injection. The original control system was manual but after two occurrences of high temperature sterilization due to excessive steam flow rates, the system was automated.

The effluent from the aeration tank flows by gravity to the center well of the final clarifier for removal of biological solids. The clarifier is a cylindrical steel tank with a cone bottom. It has an overflow of 200 gal./day/ft^2. and an effective detention time of 150 minutes at 1 gpm. The clarifier is equipped with a scum baffle, a vee notch peripheral weir, and spiral sludge rakes. The settled solids are returned to the aeration tank with a variable capacity pump. Recycle rates are manually controlled between 0 and 1 gpm. The original system was designed so that excess sludge could be wasted by periodically diverting the recycle sludge to the sewer. This approach proved unsatisfactory and was later replaced with a system of periodically draining a known percentage of mixed liquor from the aeration tank to the sewer.

The effluent from the first module flows by gravity to a 55-gallon surge tank. This partially treated waste is pumped from the surge tank to the second treatment module for aerobic oxidation of ammonia to nitrate (nitrification). The nitrification system consists of a completely mixed aeration tank, a final clarifier, and a pH control system. Equipment details are listed in Table 3.

The aerator-clarifier system in module two is identical to that described for the first module with exception that a larger mixer-aerator (15 horsepower) was supplied to adequately handle the greater oxygen demand anticipated in this system.

A pH control system consisting of a 55-gallon caustic storage tank and a positive displacement metering pump was provided to maintain the pH between 7.0 and 8.5 in the nitrification system. Caustic is metered into the aeration tank at a manually controlled rate to neutralize the nitric acid produced by the oxidation of ammonia. Dry sodium carbonate is added in batch quantities to the aeration tank to supply the nitrifying organisms with inorganic carbon.

The effluent from the nitrification system flows to a 55-gallon surge tank. The nitrified waste is pumped from the surge tank to the third treatment module for anaerobic reduction of nitrate to nitrogen gas (denitrification). The denitrification system consists of a completely mixed anaerobic growth tank, a final clarifier, and an organic carbon addition system. Equipment details are listed in Table 3.

The growth tank is a steam heated, cylindrical steel tank with a detention time of 8 hours at 1 gpm. It is equipped with a 1/2 horsepower mixer to maintain a completely mixed condition.

The final clarifier and sludge handling system is identical to the first and second modules.

A system for the addition of organic carbon (molasses, methanol, or sugar solutions) to the growth tank was provided. The system consists of a 55-gallon mix tank with a 1/4 horsepower mixer, a 55-gallon pump tank and a positive displacement metering pump. The organic carbon compound is diluted and mixed with water in the mix tank. This solution is transferred to the pump tank by gravity and metered at a manually controlled rate to the growth tank.

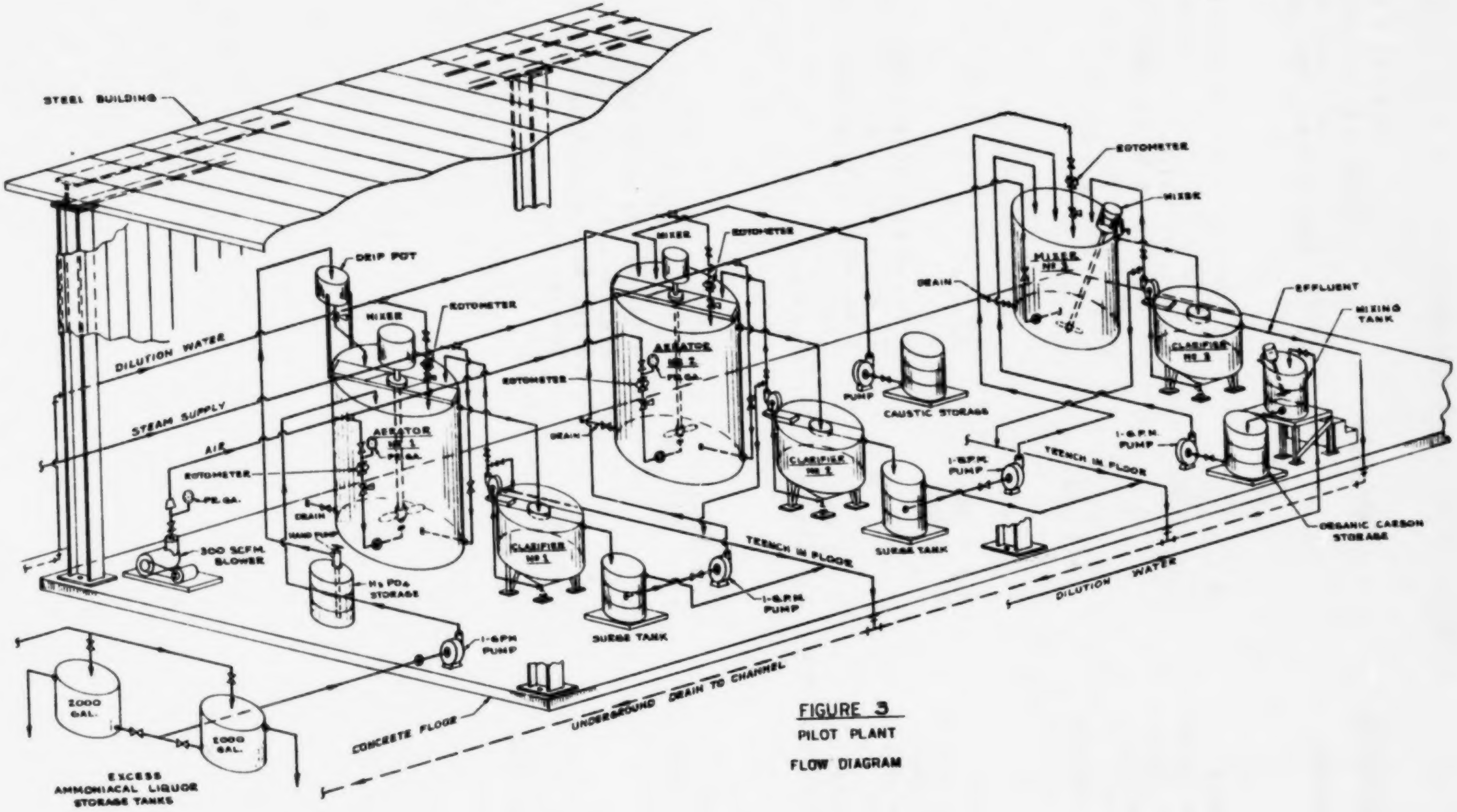
STEEL BUILDING
DRIP POT
MIXER
ROTOMETER
DILUTION WATER
STEAM SUPPLY
AIR
AERATOR No 1
PR. GA.
ROTOMETER
DRAIN
HAND PUMP
300 SCFM. BLOWER
PR. GA.
H₃ PO₄ STORAGE
1-GPM PUMP
CLARIFIER No 1
SURGE TANK
1-GPM. PUMP
TRENCH IN FLOOR
MIXER
ROTOMETER
AERATOR No 2
PR. GA.
ROTOMETER
DRAIN
CLARIFIER No 2
PUMP
CAUSTIC STORAGE
SURGE TANK
1-GPM. PUMP
TRENCH IN FLOOR
ROTOMETER
MIXER
MIXER No 3
DRAIN
CLARIFIER No 3
EFFLUENT
MIXING TANK
1-GPM. PUMP
ORGANIC CARBON STORAGE
DILUTION WATER
2000 GAL.
2000 GAL.
EXCESS AMMONIACAL LIQUOR STORAGE TANKS
CONCRETE FLOOR
UNDERGROUND DRAIN TO CHANNEL

FIGURE 3
PILOT PLANT
FLOW DIAGRAM

TABLE 3: PILOT PLANT EQUIPMENT

Equipment	Feed Rate	Size	Volume
Storage Tanks	-	6 ft. dia. x 8 ft. SWD	2000 gal.
Module I			
Waste Feed	0 - 1 gpm	1/4 hp	-
Dilution Water	0 - 1 gpm	-	-
Aeration Tank	-	5 ft. dia. x 12 ft. SWD	1500 gal.
Mixer-Aerator	-	3 hp	-
Clarifier	-	3 ft. dia. x 3 ft. SWD	150 gal.
Sludge Recycle	0 - 1 gpm	1/4 hp	-
Module II			
Waste Feed	0 - 1 gpm	1/4 hp	-
Dilution Water	0 - 1 gpm	-	-
Aeration Tank	-	5 ft. dia. x 12 ft. SWD	1500 gal.
Mixer-Aerator	-	15 hp	-
Clarifier	-	3 ft. dia. x 3 ft. SWD	150 gal.
Sludge Recycle	0 - 1 gpm	1/4 hp	-
Caustic Addition Pump	5 - 1750 ml./min.	1/6 hp	-
Module III			
Waste Feed	0 - 1 gpm	1/4 hp	-
Dilution Water	0 - 1 gpm	-	-
Growth Tank	-	4 ft. dia. x 6 ft. SWD	500 gal.
Mixer	-	1/3 hp	-
Clarifier	-	3 ft. dia. x 3 ft. SWD	150 gal.
Sludge Recycle	0 - 1 gpm	1/4 hp	-
Organic Carbon Addition Pump	5 - 1750 ml./min.	1/6 hp	-

Each of the three modules is provided with independent control of waste volumes and concentrations. Volume control is provided by 0 to 1 gpm variable capacity pumps supplying waste to each system. Dilution water for adjustment of waste concentration is also supplied to each system. Dilution water rates of 0 to 1 gpm can be metered into any of the mix tanks by a manually adjusted flow control system. The control system consists of a rotometer and a flow control needle valve. The use of these two control systems allows variations to influent flow from zero to maximum design capacity and simultaneous variations in influent concentration from zero to full waste strength.

Coke plant waste water is deficient in phosphorus and will not support biological activity without phosphorus addition.(48, 50, 63, 64) A system was installed to continuously feed phosphoric acid to the first module aeration tank. The system consisted of a 5-gallon drip pot with a discharge needle value for the continuous feed of 75% phosphoric acid. From pilot plant start up, this system was plagued with needle valve plugging problems. The system was later abandoned and replaced with a procedure for batch additions of phosphoric acid to the storage tanks at an approximate rate of 3 milliliters per 4 gallons of undiluted waste. This approach proved satisfactory and much more reliable.

SECTION VII

SAMPLING AND ANALYSIS

The sampling and analysis program conducted during the pilot plant study was designed to provide: (1) data required for routine plant operation and control; and (2) detailed data on waste loading, material balance and process efficiency. This information was obtained from analysis of samples taken from twelve sample points as shown in Figure 4. Samples from each of these points were collected regularly by the plant operator. Those analyses and measurements required for routine operation were performed by the operator in the pilot plant laboratory. Those analyses which established plant performance and efficiency but were not required for routine operation were analyzed in a remote analytical laboratory. The sampling and analysis schedule used throughout the study is shown in Table 4.

Analyses and measurements performed by the operator for routine control of the pilot plant included flow rates, temperature, dissolved oxygen, settleable solids, alkalinity, pH, and dissolved solids. For convenience and simplicity the biological solids level was determined indirectly by the measurement of settleable solids. Periodic analysis of suspended solids were used to correlate settleable solids data with the more conventional mixed liquor suspended solids.

In addition to the measurements and analyses performed as a part of normal plant operation, a supplemental analytical program was conducted at a remote laboratory. This program was designed to determine waste loadings, material balances and treatment efficiencies. Samples collected at the pilot plant were preserved by refrigeration during storage and shipment. Generally, the analytical work was in progress within four hours of sample collection. All analyses were performed in accordance with the recommendations of the 12th edition of Standard Methods for the Examination of Water and Waste Water.

The first treatment module was designed for removal of organic carbon and cyanide compounds. Total organic carbon and cyanide were selected, therefore, as indicators of waste loading and treatment efficiency. Influent and effluent analyses for the indicator materials were performed three days each week. Difficulties with obtaining reproducible total organic carbon results during the initial part of the study resulted in the conversion from this analysis to chemical oxygen demand (C.O.D.). In addition to the indicator materials, regular analysis (weekly or more frequently) for phenolics, thiocyanate, sulfide, ammonia, and organic nitrogen were performed so that loadings and treatment efficiencies for these materials could be determined.

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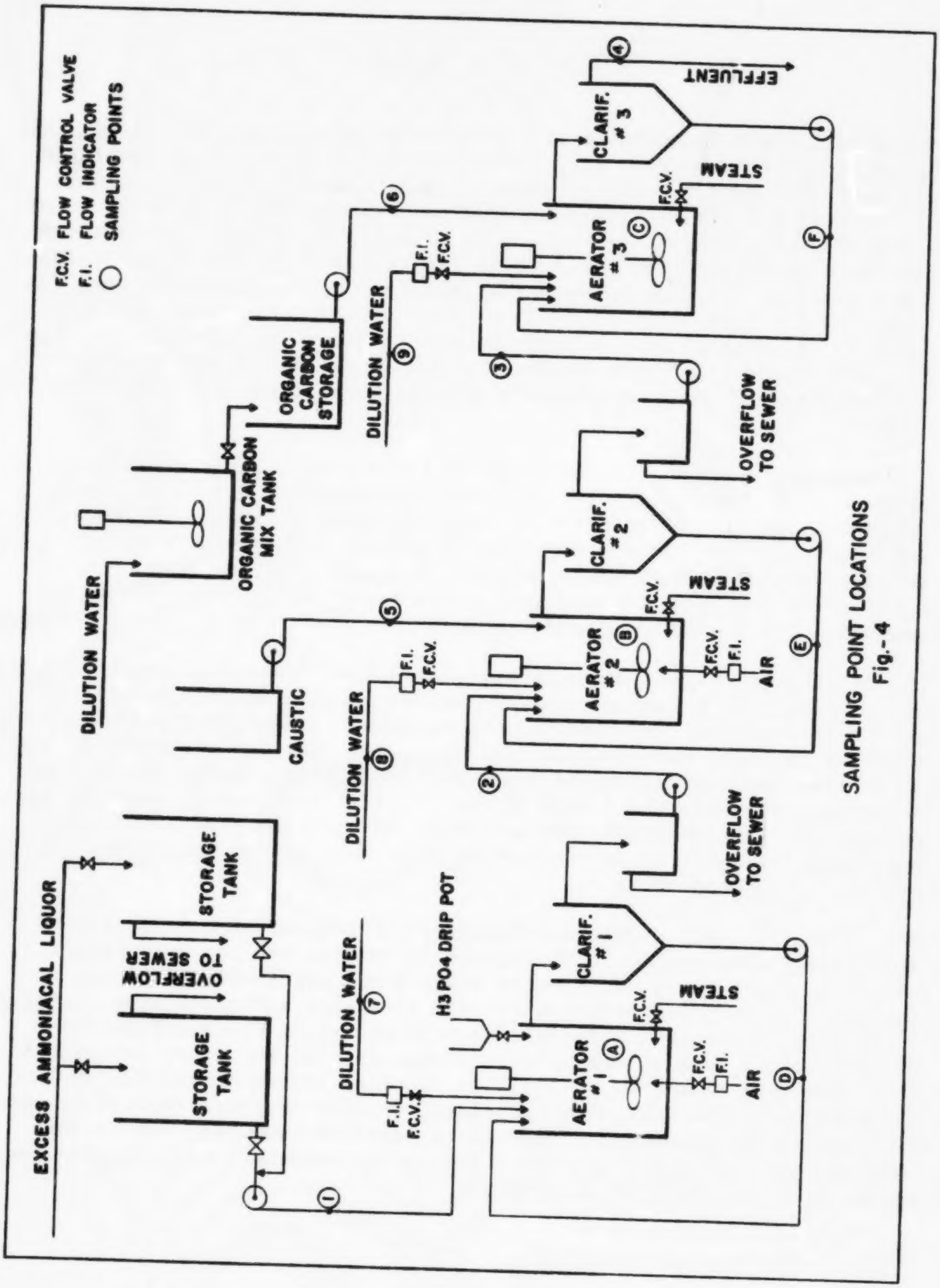
F.C.V. FLOW CONTROL VALVE
F.I. FLOW INDICATOR
○ SAMPLING POINTS
EXCESS AMMONIACAL LIQUOR
STORAGE TANK
OVERFLOW TO SEWER
STORAGE TANK
1
DILUTION WATER
7
F.I.
F.C.V.
H3 PO4 DRIP POT
AERATOR #1
A
F.C.V.
F.I.
AIR
D
F.C.V.
STEAM
CLARIF. #1
OVERFLOW TO SEWER
2
DILUTION WATER
8
F.I.
F.C.V.
CAUSTIC
5
AERATOR #2
B
F.C.V.
F.I.
AIR
E
F.C.V.
STEAM
CLARIF. #2
OVERFLOW TO SEWER
DILUTION WATER
ORGANIC CARBON MIX TANK
ORGANIC CARBON STORAGE
DILUTION WATER
9
F.I.
F.C.V.
6
3
AERATOR #3
C
F.C.V.
STEAM
F
CLARIF. #3
4
EFFLUENT

SAMPLING POINT LOCATIONS
Fig.-4

TABLE 4

SAMPLING AND ANALYSIS SCHEDULE

Parameters	Sampling Location																									
	1				2			3			4				5	6	7	8	9	A		B		C	
	Sampling Interval[1]																									
	D	A	W	P	D	A	W	D	A	W	D	A	W	P	D	D	D	D	D	A	P	A	P	A	P
Flow	X				X			X			X				X	X	X	X	X						
Temperature	X				X			X			X														
Seechi Disc or Equivalent					X			X			X														
pH	X				X			X			X														
Conductivity	X				X			X			X														
Alkalinity	X				X			X			X														
Dissolved Oxygen																				X		X		X	
Suspended Solids																					X		X		X
Settable Solids																				X		X		X	
Total Organic Carbon		X				X			X			X													
COD		X				X																			
BOD-5				X										X											
Phenolics			X				X																		
Cyanides		X				X																			
Thiocyanates			X				X																		
Sulfides			X				X																		
Ammonia		X				X			X			X													
Organic Nitrogen			X				X						X												
Nitrite										X			X												
Nitrate						X			X			X													
Phosphate				X										X											

1. D - Daily
   A - Alternate Days (Mon., Wed., Fri.)
   W - Weekly
   P - Periodically

The second treatment module was designed for oxidation of ammonia to nitrate and nitrite followed by the reduction of these compounds in the third module to nitrogen gas. As an indication of waste loading and treatment efficiency influent and effluent samples from both modules were analyzed three times each week for ammonia, nitrate, and nitrite. To provide a more complete nitrogen balance across the system, organic nitrogen was also determined routinely.

SECTION VIII

OPERATIONS AND RESULTS

The operation for almost one year of the three-stage pilot plant resulted in the collection of much detailed data. The experiment by its very design was unsteady and when combined with variations in waste characteristics and operating difficulties make data interpretations difficult and somewhat uncertain. However, in this section an attempt will be made to present the chronology of operations, the data from the three operational treatment stages (carbonaceous removal, nitrification, and denitrification) and to discuss the results obtained in relationship to operating conditions. Because of the many variables and the dependency of the succeeding operating units on previous treatment operations, this section will present the data and discussion of each unit in the sequence in which they were operated.

Most of the discussion in this section will be based on summarized data to be found within this section. More complete analytical data sets are provided in the appendixes to this report. Summarized or averaged data is used because it reduces both the variability of the data and because it reduces to manageable dimensions the problem of presenting and interpreting the results. Two methods of selecting averaging periods were used for the data. During the early portion of the test, averaging periods were chose to represent periods in which a single batch of waste was used as the plant influent. This period was characterized by use of high dilution rates which allowed the use of a uniform influent (one filling of a storage tank) for periods of several days. This permitted the averaging of several determinations for most variables. As dilution rates decreased, the time required to empty a waste storage tank decreased to little more than one day. During these intervals an arbitrary averaging period of about one week was selected.

In the tables to follow, the averaging period for the successive stages of operation have been selected so as to represent as closely as possible a slug of waste passing through the treatment complex. In other words, as a first approximation, the averaging periods have been selected to represent periods corresponding to the delay based on detention times. Thus, the averaging period for the nitrification and denitrification unit lag by one and two days, respectively, the period selected for the carbonaceous unit because of the 24-hour detention times used in both the first and second treatment units. The numbers used for designating the operational periods in the tables of this section are days of operation counting from 1 February 1970.

THE EXCESS AMMONIACAL LIQUOR

Before proceeding with a discussion of each of the sequential treatment units, a description of the character of waste itself through the experiment is necessary. Waste strength and variability are most important parameters in the operation of biological treatment systems. The characteristics of the waste for the averaging periods are given in Table 5 and a summary for the major characteristics of the waste are given in Table 6. (Detailed data is included in Appendix A-1.) These results show the waste to be highly variable in chemical oxygen demand, phenolics, thiocyanate, sulfides, and organic nitrogen, but less so in ammonia. Actually of more importance to waste treatment than simply the variability of waste strength is the rate of change in the concentrations of the constituents. From Table 5, it is apparent that changes from one averaging period to another can exceed a factor of 2 for COD and approach this factor for phenolics, thiocyanate, and ammonia. These variations must be dampened prior to entry into a biological plant if overloads and underloads are to be avoided.

An important criterion for the operation of biological systems treating excess ammoniacal liquor is the percentage of liquor being treated. Influent dilution factor is one of the major controls the operator has on the system. Two approaches are available for estimating the actual dilution rate used at a specific time. First, the operator attempted to establish a specified dilution rate by pump adjustments and monitored the flow rates for both the liquor and dilution water (given in Appendix B-1). However, because of variations in flows, a better estimate of actual dilution rates was possible through the use of a materials balance computation for conductivity. Conductivity was chosen because it is a conservative constituent, that is, the concentration is not affected significantly by the treatment. In addition, the large difference between the conductivities of the waste and the dilution water makes the computation more reliable. Since conductivity is a measure of dissolved solids, the conductivity in and out of the treatment system is hypothesized to be equal. This may be written as

$$Q_D C_D + Q_L C_L = (Q_D + Q_L) C_E \qquad (1)$$

where

Q_D = quantity of dilution water,
Q_L = quantity of liquor,
C_D = conductivity of dilution water,
C_L = conductivity of liquor, and
C_E = conductivity of the effluent,

TABLE 5 - EXCESS AMMONIACAL LIQUOR

PERIOD	pH	ALKALINITY mg/1 CaCO$_3$	CONDUCTIVITY µmhos	ORGANIC CARBON mg/1 C	COD mg/1 O$_2$	BOD-5 mg/1 O$_2$	PHENOLICS mg/1 PHENOL	CYANIDE mg/1 CN	THIOCYANATE mg/1 SCN	SULFIDES mg/1 S	AMMONIA mg/1 N	ORGANIC NITROGEN mg/1 N	TOTAL NITROGEN mg/1 N
1-5 2/1-5	8.5	1330	15400	700			500	10	250	0	1860	100	1970
6-13 2/6-13	8.7	1630	14100	720			410	23	210	7	1910	115	2040
14-21 2/14-21	8.9	2540	10900	760			500	32	190	50	1800	90	1910
22-29 2/22-3/1	8.7	1760	12800	760			525	27			1920		--
30-39 3/2-11	8.8	1970	12200	730			530	22	250	22	1900	90	2000
40-43 3/12-15	8.7	1520	13900	1370			780	17	250	4	1960	100	2070
44-48 3/16-20	8.4	1220	14250	1450	3630	2330	765	10	240	0	1890	90	1990
49-55 3/21-27	8.7	1600	16700	1480			645	15	290	0	1780	100	1890
56-57 3/28-29	9.1	2700	13300	1140				37			2250		--
59-60 3/30-4/1	8.9	2630	14200	1700				16			2010		--
61-67 4/2-8	8.8	2170	12500	2360			930	21	175	23	1960	70	2040
69-73 4/9-14	8.6	1910	12100	2030			730	28	240	2	1880		--
74-76 4/15-17	8.5	1730	21000	2970				25			3110		--
77-81 4/18-22	8.4	1680	24450	3700			1330	26	390	2	3570	250	3830
82-84 4/23-25	8.5	1560	26400	2660				21			4170		--
85-88 4/26-29	8.4	1360	23400	1990			850	21	550	0	3500	200	3710
89-91 4/30-5/2	8.4	1340	23900	1920				24			3740		--
92-95 5/3-6	8.5	1420	21200	1260	3400	1710	560	28	400	2	3200	120	3340
96-98 5/7-9	8.6	2100	20000	1670				30			3490		--
99-103 5/10-14	8.6	1440	20600	1650			665	32	360	3	3350	200	3570
104-108 5/15-19	8.6	1660	23400	1510				35			3630		--
109-112 5/20-23	8.5	1750	20700	1600			850	24	230	3	3400	190	3600
113-116 5/24-27	8.6	1780	21300	930			530	36	100	6	3400	225	3640
117-121 5/28-6/1	8.6	1820	18900	1070				30			3100		--
122-129 6/2-9	8.6	2000	20700	1700			700	36	410	0	3400	15	3440
130-136 6/10-16	8.6	1590	24200	1200			900	30	360	0	3850	375	4240
137-143 6/17-23	8.6	1440	29400	510	2920		650	23	290	0	3880	180	4070
144-150 6/24-30	8.5	1630	24600	460	3460		650	25	370	0	3740	180	3930
151-157 7/1-7	8.4	1300	25800	720	3360	1830	580	28	350	0	3620	180	3820
158-164 7/8-14	8.4	1390	26200		3170		490	27	300	0	3620	150	3780
165-171 7/15-21	8.3	1230	26500		2900		540	27	310	0	3530	260	3800
172-178 7/22-28	8.4	1400	24700		2830		-	26	-	-	3270	-	--
179-185 7/29-8/4	8.4	1450	22700	1290	2460		420	26	300	2	3170	100	3280
186-192 8/5-11	8.5	1430	19600		2700		500	23	320	0	2720	110	2840
193-199 8/12-18	8.6	1500	20000		2930		550	25	290	4	2840	120	2970
200-206 8/19-25	8.5	1690	21300	880	3260		710	21	430	2	3040	140	3190
207-213 8/26-9/1	8.6	1650	15000		3350		1240	22	140	2	2200	140	2350
214-220 9/2-8	8.6	1830	21500		7670		1700	13	530	1	3030	150	3190
221-227 9/9-15	8.6	2290	28500		9230	6170	1860	14	770	1	4180	230	4420
228-234 9/16-22	8.6	2230	28500		9010		1900	19	1540	1	4120	200	4330
235-241 9/23-29	8.6	2290	22300		9120		2150	18	630	2	3350	170	3530
242-248 9/30-10/6	8.6	2610	26500		10400	5790	2380	22	1100	2	4020	190	4220
249-255 10/7-13	8.6	2510	28000		9600		650	19	660	4	3960	260	4230
256-262 10/14-20	8.7	2190	27500		9720		-	10	-	-	3780	-	--
263-269 10/21-27	8.7	2120	29300		8180		950	18	580	0	4200	230	4440
270-276 10/28-11/3	8.6	1630	26300		5420	2460	920	25	550	3	3630	200	3840
277-283 11/4-10	8.6	1840	29200		3660		1070	35	640	2	4070	200	4290
284-290 11/11-17	8.7	1890	27600		5770		1080	20	540	3	3750	90	3850
291-297 11/18-24	8.6	1880	25300		5140		1110	18	560	1	3610	150	3760
298-304 11/25-12/1	8.4	1540	28900		5750		1120	20	350	0	3850	170	4030
305-311 12/2-8	8.5	1590	22600		3660	3160	1480	15	690	1	3810	260	4080
312-318 12/9-15	8.7	2370	29900		6690		1190	32	650	4	4190	180	4390
319-325 12/16-22	8.6	1970	31800		5710		1100	26	640	1	4290	250	4550
326-332 12/23-29	8.6	1990	29200		6520		1290	23	650	4	2500	700	3200
333-339 12/30-1/5	8.7	2190	29700		4750	4030	1350	17	670	1	2020	2300	4330
340-346 1/6-12	8.7	2350	31200		5130		1010	22	610	2	2060	2100	4150
347-353 1/13-19	8.7	2390	29300		5830		1200	25	650	2	3790	80	3880

Since the only contributors of solids and liquids to the system are the dilution water and the liquor and neglecting any losses in the blowdown, this equation can easily be reduced to give for the fraction of liquor being treated,

$$\frac{Q_L}{Q_L + Q_D} = \frac{C_E - C_D}{C_L - C_D} \qquad (2)$$

The solution of this equation requires the knowledge of the conductivities of the dilution water, liquor, and effluent for each averaging period. Values of the conductivities for the liquor are given in Appendix A-1 and for the effluent from the carbonaceous unit in Appendix A-2. The conductivity of the dilution water was by comparison low and was relatively constant throughout the test. A constant value of 600 micromhos per cm. has been assumed for the conductivity of the dilution water.

TABLE 6: SUMMARY OF CHARACTERISTICS - EXCESS AMMONIACAL LIQUOR

Parameter	Mean	Median	Standard Deviation	Range
pH		8.6		8.3-9.1
Alkalinity mg/l $CaCO_3$	1800	1700	390	1200-2700
Conductivity umhos/cm^2	23000	23000	5800	11000-32000
COD mg/l O_2	5800	5700	2500	2500-10000
Phenolics mg/l Phenol	950	850	460	410-2400
Cyanide mg/l CN	24	23	6	10-37
Thiocyanate mg/l SCN	470	380	260	100-1500
Sulfides mg/l S	3.7	2	8.2	0-50
Ammonia mg/l N	3200	3400	800	1800-4300
Organic N mg/l N	270	180	430	15-2300

CARBONACEOUS TREATMENT UNIT

The carbon removal unit began operation on 8 January 1970 when an influent flow of one (1) gallon per minute of a 15 percent dilution of excess ammoniacal liquor was initiated. This flow rate represented an aeration time of approximately 24 hours. Phosphoric acid was added according to the schedule given in Section VI. The system was seeded on 8 January with unknown quantities of three different materials, Bethlehem Steel biological solids, soil from in and around the Houston Coke Plant by-products area, and final clarifier sludge from the Houston Works trickling filter sewage plant. Unfortunately, the system was pasteurized on 15 January by the accidental increase in aeration tank temperature above 150° F. The system was restarted on 16 January and seeded with the same materials previously used.

The remainder of the month of January was basically used for adapting organisms to the waste, accumulating organisms, and learning to operate the unit. During this period recycle flow was one (1) gallon per minute and no sludge was intentionally wasted. On 1 February collection of operating and analytical data was begun.

Table 7 summarizes the operating information for the individual averaging periods for the carbonaceous unit. More detailed information can be found in Appendix B-1. Table 8 gives the chemical composition of the influent to the unit and Table 9 gives the effluent quality, percent removals, and loadings. These three tables provide a summary of the chronology of operation, the data obtained, and the problems encountered.

The results of the computation for percentage of waste in the influent are given in both Tables 7 and 8. The original project plan called for increasing waste percentages in a consistent manner. However, because of unit upsets which will be discussed later, several reductions in liquor percentages were found to be necessary in order to maintain adequate treatment levels. A plot of the percent waste treated in the carbonaceous unit for the duration of the test is given in Figure 5.

In addition to the waste concentration being treated, Table 7 provides data on several other operational parameters. Among items of major interest are reactor temperature, pH, dissolved oxygen, and suspended solids. Also included are measures of the clarity of the effluent (Secchi disk), blowdown rate, chemical additives used and special operational conditions encountered.

TABLE 7: OPERATING CONDITIONS, CARBON REMOVAL UNIT

PERIOD	INFLUENT, PERCENT WASTE	TEMPERATURE, °F	pH	DISSOLVED OXYGEN, mg/l O_2	REACTOR SUSPENDED SOLIDS, mg/l	Imhoff Cone ml/l		SECCHI DISK, INCHES	BLOWDOWN, PERCENT/DAY	Chemical Additives per Period						Special Conditions						COMMENTS
										ml.		pounds										
						MIXED LIQUOR	RETURN SLUDGE			PHOSPHORIC ACID	TRIBUTYL PHOSPHATE	LIMESTONE	BURNT LIME	HYDRATED LIME	SODIUM CARBONATE	FOAM	FROTH	DISSOLVED OXYGEN	TEMPERATURE	FLOW	RETURN SLUDGE	
1-5	13	80	8.3			0	3													X		3 ml per 4 gals. undiluted waste, phosphoric acid.
6-13	15	76	8.3			5	18	8		See Comment												
14-21	17	79	8.0			10	21	7														
22-29	15	80	8.2			19	40	8	2													
30-39	15	82	7.8			36	63	11	2													
40-43	16	77	6.6			73	140	9	2													
44-48	16	80	6.4			49	100	9	2			3			1					X		
49-55	15	78	7.5			70	170	6	2-6						2		X				X	
56-57	22	80	7.5					6	4-6					2	4		X					
58-60	29	81	7.0			62	140	5	4					1/2			X					
61-67	23	82	7.8			41	63	5	2-6	750					5	X	X		X			(64) Temp.= 123°F.
68-73	27	80	8.5			34	49	4	2		30					X						
74-76	25	81	8.3			34	94	5	2		50									X	X	
77-81	34	82	8.1			36	340	3	2								X					
82-84	16	85	8.1			190	740	4	2		100					X	X					
85-88	42	85	8.1			180	400	4	2							X				X		
89-91	38	79	7.8			200	400	3	2		125					X						
92-95	47	76	7.6			170	290	3	2		125									X		
96-98	61	79	8.3			160	600	3	2							X						
99-103	64	86	8.3			210	610	4	2							X						
104-108	57	83	8.2	2.7		260	700	4	2													
109-112	70	85	8.2	3.7		210	540	3	2	750	150					X				X		
113-116	76	86	8.2	4.1		180	380	4	2	1500	250									X		
117-121	73	86	8.3	2.8		180	360	4	2	1300	225											
122-129	82	84	8.3	2.3		130	240	2	2-6	2900	570									X		
130-136	89	90	8.3			80	125	2	2-6	2800	450					X	X			X		D.O. not available.
137-143	56	89	8.2	2.0		45	90	2	2	2200								X				(136) D. O. = 0.2 mg/l.
144-150	65	89	8.1	1.9		50	100	3	2	1500	100					X	X			X		
151-157	60	88	8.0	2.1		39	78	3	2	2200	300											
158-164	54	89	8.0	2.3		53	108	3	2	2200	300						X			X		
165-171	49	88	8.0	2.2		57	79	3	2	2200	300						X					
172-178	72	87	8.1	1.7		84	180	3	2	3000	500					X		X		X		(173) D.O. = 0.1 mg/l.
179-185	78	90	7.9	1.6		160	210	4	2	1500	300					X	X			X		
186-192	74	91	8.1	1.9		120	240	3	2	2200	500											
193-199	74	88	8.2	1.7		140	220	3	2	1500	300							X		X		(199) D.O. = 0.5 mg/l.
200-206	74	89	8.2	1.0		70	210	2	0	1500	300							X		X		D. O. marginal.
207-213	86	85	8.0	1.9		140	210	2	0.5	2200	300									X		
214-220	71	89	7.9	1.2	1420	170	310	2	1	2200	400					X				X		
221-227	68	90	7.9	1.0	1220	160	280	2	1	2200	500					X	X	X		X		(223) D.O. = 0.3 mg/l.
228-234	79	90	7.8	1.3		140	190	2	0.5	2200	600									X		
235-241	81	84	7.9		700	40	30	2	0.5	1500	400					X						
242-248	75	78	8.0	0.8		8	8	2		3000	800					X				X		D. O. marginal
249-255	40	78	8.0	2.7		8	8	2		750	100				2							
256-262	17	75	8.1	2.3		2	2	2		750	100											System reseeded.
263-269	21	82	8.0	4.8		4	3	2									X					
270-276	41	72	8.1	3.0	150	15	16	2		1500	300					X				X		
277-283	47	72	8.2	2.3		12	16	2		2200	500								X	X		(278) Temp.= 64°F.
284-290	58	70	8.2	2.3		3	6	2		1500	300						y		X			(289) Temp.= 61°F.
291-297	30	71	8.2	2.8	100	1	5	3		750	150								X			(297) Temp.= 62°F.
298-304	22	77	8.1	2.5	140	4	5	4		1500	300											
305-311	35	89	8.1	1.0		65	90	4		750	150					X						Heating reactor.
312-318	45	90	8.2	2.4	850	190	330	3		750	150					X						
319-325	45	86	8.2	2.0		180	360	3		2200	400						X			X		
326-332	58	88	8.1	2.0		220	400	3		1500	300											
333-339	49	89	8.3	2.0		280	450	3		1500	200									X		
340-346	46	91	8.2	2.2		260	430	2		1500	200									X		
347-352	57	86	8.2			260	560	2		1500	300					X	X					

TABLE 8: INFLUENT, CARBON REMOVAL UNIT

PERIOD 1970-71	PERCENT WASTE	ORGANIC CARBON, mg/l C	COD mg/l O_2	BOD-5 mg/l O_2	PHENOLICS mg/l PHENOL	CYANIDE mg/l CN	THIOCYANATE mg/l SCN	AMMONIA mg/l N	ORGANIC NITROGEN mg/l N	TOTAL NITROGEN mg/l N	PHOSPHATE mg/l P
1-5 2/1-5	13	90			66	1.3	33	240	13	250	
6-13 2/6-13	15	110			60	3.5	32	290	17	310	
14-21 2/14-21	17	130			85	5.5	32	310	15	330	
22-29 2/22-3/1	15	115			80	4.1		290			
30-39 3/2-11	15	110			80	3.4	37	280	13	290	
40-43 3/12-15	16	220			120	2.7	40	310	17	330	
44-48 3/16-20	16	230	580	370	120	1.6	38	300	14	310	
49-55 3/21-27	15	220			100	2.2	43	270	15	290	
56-57 3/28-29	22	250				8.1		500			
58-60 3/30-4/1	29	500				4.6		580			
61-67 4/2-8	23	550			210	4.9	40	450	16	470	
68-73 4/9-14	27	550			200	7.7	65	510			
74-76 4/15-17	25	740				6.4		780			
77-81 4/18-22	34	1260			450	8.9	130	1210	86	1300	
82-84 4/23-25	36	950				7.7		1500			
85-88 4/26-29	42	840			350	8.8	230	1470	84	1550	
89-91 4/30-5/2	38	730				9.1		1420			
92-95 5/3-6	47	590	1600	800	260	13.4	190	1500	56	1560	44
96-98 5/7-9	61	1020				18.3		2130			
99-103 5/10-14	64	1050			430	20.4	230	2140	125	2270	
104-108 5/15-19	57	860				20.0		2070			
109-112 5/20-23	70	1120			590	16.8	160	2390	130	2520	
113-116 5/24-27	76	710			480	27.4	75	2590	170	2750	
117-121 5/28-6/1	73	780				21.9		2260			
122-129 6/2-9	82	1390			570	29.6	340	2780	10	2790	
130-136 6/10-16	89	1070			800	26.7	320	3420	330	3750	
137-143 6/17-23	56	290(?)	1640		360	12.9	160	2180	100	2280	
144-150 6/24-30	65	300(?)	2250		420	16.2	240	2440	120	2560	61
151-157 7/1-7	60	430	2000	1100	350	17	210	2170	110	2280	
158-164 7/8-14	54		1710		260	15	160	1960	80	2040	
165-171 7/15-21	49		1420		260	13	150	1730	130	1860	
172-178 7/22-28	72		2060		-	19	-	2360	-	--	
179-185 7/29-8/4	78	1000	1920		330	20	230	2480	80	2560	50
186-192 8/5-11	74		2000		370	17	240	2020	80	2100	
193-199 8/12-18	74		2170		410	18	210	2100	90	2200	
200-206 8/19-25	74	650	2400		530	16	320	2300	100	2400	
207-213 8/26-9/1	86		2880		1100	19	120	1900	120	2020	
214-220 9/2-8	71		5500		1200	9	380	2200	110	2310	
221-227 9/9-15	68		6300	4200	1260	9	520	2800	160	2960	49
228-234 9/16-22	79		7100		1500	15	1200	3260	160	3420	
235-241 9/23-29	81		7400		1750	15	510	2700	140	2850	
242-248 9/30-10/6	75		7800	4300	1800	16	820	3000	140	3140	
249-255 10/7-13	40		3800		260	8	260	1600	100	1700	0.8
256-262 10/14-20	17		1650		-	2	-	640	-	--	
263-269 10/21-27	23		1900		220	4	110	960	50	1010	
270-276 10/28-11/3	43		2320	1050	400	10	230	1560	90	1650	34
277-283 11/4-10	47		4100		500	16	300	1900	100	2000	
284-290 11/11-17	58		3350		630	12	310	2170	50	2220	
291-297 11/18-24	30		1550		330	5	170	1080	40	1120	
298-304 11/25-12/1	22		1260		250	4	80	850	40	890	60
305-311 12/2-8	35		3030	1460	520	6	240	1340	80	1420	
312-318 12/9-15	45		3000		520	14	290	1890	80	1960	
319-325 12/16-22	45		2570		500	12	290	1930	110	2040	
326-332 12/23-29	58		3800		750	13	380	1440	410	1850	
333-339 12/30-1/5	49		3300	1980	640	8	330	1000	1130	2130	
340-346 1/6-12	46		2680		470	10	290	940	970	1910	
347-352 1/13-18	47		2740		560	12	310	1780	40	1820	

TABLE 9: LOADINGS AND REMOVALS, CARBON REMOVAL UNIT

PERIOD	ORGANIC CARBON			CHEMICAL OXYGEN DEMAND			PHENOLICS		CYANIDE			THIOCYANATE			AMMONIA		TOTAL N	
	Effluent mg/l C	Influent Loading Parameter	% Removal	Effluent mg/l O_2	Influent Loading Parameter	% Removal	Effluent mg/l Phenol	Influent Loading Parameter	Effluent mg/l CN	Influent Loading Parameter	% Removal	Effluent mg/l SCN	Influent Loading Parameter	% Removal	Effluent mg/l N	% Removal	Effluent mg/l N	% Removal
1-5 2/1-5	32	230	64				0.1	170	0.6	3	54	32	82	0	200	17	230	18
6-13 2/6-13	27	20	65				0.2	11	0.9	0.6	74	39	6	0	265	9	300	3
14-21 2/14-21	30	14	77				0.2	9	0.7	0.6	87	26	2	20	240	24	270	18
22-29 2/22-3/1	20	6	82				0.4	4	0.9	0.2	78	35			220	24	240	
30-39 3/2-11	18	3	84				0.1	2	1.1	0.1	68	22	1	40	200	28	280	4
40-43 3/12-15	22	3	90				0.1	2	2.1	0.04	22	17	1	57	210	33	320	3
44-48 3/16-20	16	5	93					2	3.4	0.03			1		200	34		
49-55 3/21/27	19	3	91					1	2.0	0.03	10		1		230	16		
56-57 3/28-29	25		90				0.0		1.3		84	12			280	35	360	
58-60 3/30-4/1	35	8	93						3.2	0.07	30				410	30		
61-67 4/2/8	144	13	71				124	5	1.6	0.1	67	86	1		320	30	350	25
68-73 4/9-14	47	16	91				0.2	6	1.1	0.2	86	64	2	0	340	34	380	
74-76 4/15-17	44	22	94						1.5	0.2	77				600	23		
77-81 4/18-22	94	35	93				0.1	12	4.1	0.2	54	79	4	40	950	21	1000	23
82-84 4/23/25	66	5	93						4.9	0.04	36				1220	19		
85-88 4/26-29	82	5	90				0.2	2	3.2	0.05	64	113	1	50	1260	14	1300	16
89-91 4/30-5/2	66	4	91						2.7	0.05	70				1190	16		
92-95 5/3-6	57	3	90				1.0	2	3.6	0.08	73	22	1	88	1290	15	1350	19
96-98 5/7-9	150	6	85						5.8	0.01	68				1700	20		
99-103 5/10-14	53	5	95				0.1	2	7.6	0.09	63	164	1	30	1580	26	1660	27
104-108 5/15-19	140	3	84				0.2		4.7	0.07	76	86			1780	14	1890	
109-112 5/20-23	62	5	94					3	10	0.08	40		1		1970	17		
113-116 5/24/27	48	4	93				0.2	3	20	0.2	26	198			2370	8	2580	6
117-121 5/28-6/1	90	4	88				5.0		5.2	0.1	76	180			1740	23	1800	
122-129 6/2-9	130	10	91				0.6	4	7.0	0.2	76		3		2500	10		
130-136 6/10-16	270	13	75	1700			0.6	10	7.0	0.3	74	340	4		2950	14	3150	14
137-143 6/17-23	40	6	86	950	36	42	0.3	8	4.9	0.3	62	240	4		1940	11	2040	10
144-150 6/24-30	24	6	92	800	45	65	0.2	6	5.2	0.3	68	154	5	35	1950	20	2060	19
151-157 7/1-7	53	11	88	700	51	65	0.2	9	8.6	0.4	50	160	5	24	1880	13	1930	15
158-164 7/8-14				690	32	60	0.2	5	4.0	0.3	73	170	3	0	1670	15	1760	14
165-171 7/15-21				620	25	56	0.2	5	3.7	0.2	72	170	3	0	1550	10	1700	9
172-178 7/22/28	41	6	-	1040	24	49	-	-	5.0	0.2	74	-	-	-	2080	12	-	-
179-185 7/29-8/4				770	12	60	0.3	2	5.6	0.1	72	190	1	17	2090	16	2210	14
186-192 8/5-11				700	17	65	0.2	3	5.0	0.1	71	250	2	0	1780	12	1860	11
193-199 8/12-18				750	15	65	0.2	3	6.0	0.1	67	220	2	0	1830	13	1920	13
200-206 8/19-25	72	9	89	1000	35	59	0.3	8	5.4	0.2	66	270	5	15	1870	19	1940	19
207-213 8/26-9/1				790	21	72	0.2	8	3.5	0.1	82	140	1	0	1480	22	1590	21
214-220 9/2-8				840	32	67	0.2	7	4.5	0.1	50	270	2	29	1850	16	1960	15
221-227 9/9-15				1740	39	73	1.0	8	4.7	0.1	48	390	3	44	2320	17	2490	14
228-234 9/16-22				2400	51	66	1.2	11	4.5	0.1	70	1220	9	0	2670	18	2820	18
235-241 9/23-29				2080	180	72	11.	44	6.7	0.3	55	390	13	24	1630	40	1800	37
242-248 9/30-10/6				2740	1000	65	16.	220	5.6	2	65	630	100	23	2340	22	2470	23
249-255 10/7-13				1550	470	59	0.2	32	3.4	1	57	150	32	32	1350	16	1450	15
256-262 10/14-20				610	820	63	-		1.7	1	15	510	-	-	510	20	-	-
263-269 10/21-27				630	480	67	0.2	55	2.1	1	48	220	27	0	760	21	950	6
270-276 10/28-11/3				770	150	67	0.2	27	4.8	0.6	52	190	15	17	1240	20	1310	21
277-283 11/4-10				1100	340	73	0.6	42	4.8	1.	70	290	25	3	1610	15	1710	15
284-290 11/11-11/17				1130	1100	66	4.3	210	9.8	4	18	310	100	0	1890	13	1950	12
291-297 11/18-24				650	1500	58	0.4	330	3.0	5	40	140	170	17	900	17	970	14
298-304 11/25-12/1				400	320	68	0.1	62	2.6	1	35	180	20	0	790	7	850	5
305-311 12/2-8				490	46	84	0.1	8	4.1	0.1	32	250	4	0	1090	19	1140	20
312-318 12/9-15				710	16	76	0.2	3	5.7	0.1	59	280	2	0	1600	15	1640	16
319-325 12/16-22				710	14	72	0.1	3	6.3	0.1	48	280	2	0	1760	9	1800	12
326-332 12/23-29				700	17	82	0.3	3	5.5	0.1	58	280	2	26	1120	22	1520	18
333-339 12/30-1/5				630	12	81	0.2	2	4.6	0.0	43	280	1	15	820	18	1750	18
340-346 1/6-12				750	10	72	0.3	2	5.1	0.0	49	290	1	0	770	18	1660	13
347-352 1/13-18				730	11	73	0.2	2	5.3	0.1	56	280	1	10	1680	6	1750	4

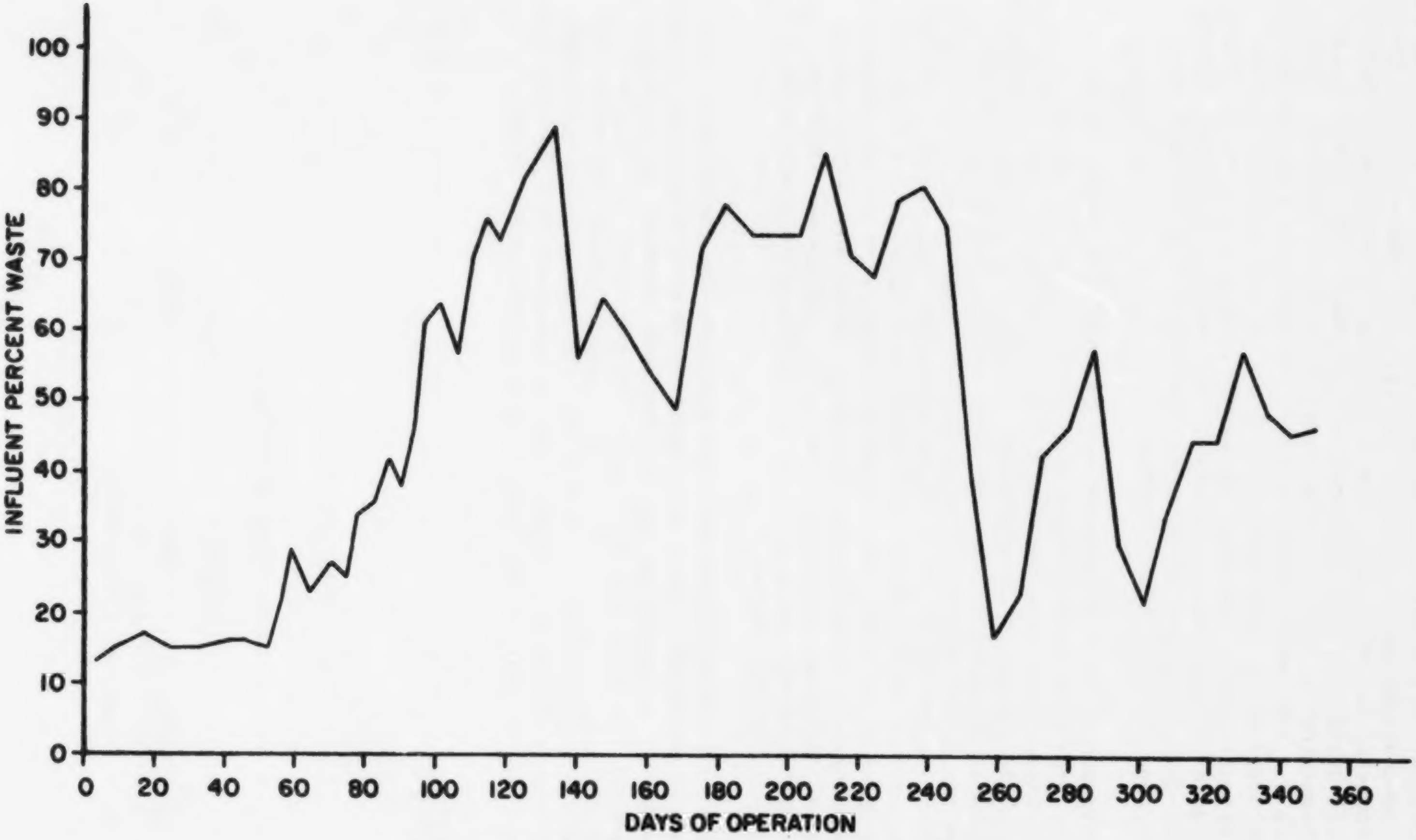

Fig.-5 - CARBONACEOUS REMOVAL UNIT
PERCENTAGE OF WASTE UNDER TREATMENT

The actual influent to the carbonaceous unit was not monitored for quality parameters. Concentrations of chemical constituents present in the influent were computed by multiplying the percentage of waste being treated by the chemical quality of the undiluted excess ammoniacal liquor being treated and tabulated in Table 5. The computed influent qualities are given in Table 8. Any contribution to these constituents from the dilution water is considered to be insignificant. Plots of the influent concentrations of organic carbon and chemical oxygen demand are given in Figure 6; phenolics, Figure 7; thiocyanate, Figure 8; and ammonia and total nitrogen, Figure 9. The abrupt changes in concentrations to which the unit was subjected are apparent from these Figures.

One of the purposes of this experiment was to determine under field conditions the operating capabilities and limits of the biological process. In other words, more realistic design parameters were being sought for the biological treatment of ammoniacal liquors than could be obtained from small laboratory experiments. For many wastes, design parameters for treatment are often determined by conducting a series of experiments using acclimated organisms in which temperature, pH, and viable organism concentration are the major variables. Ammoniacal liquor is a somewhat unique waste in that, to date, raw liquor has never been treated successfully in a biological system without dilution. Thus, the percentage of waste becomes an important parameter also. This additional variable coupled with the unsteady quality of the raw waste already mentioned made the experiment even more complex.

Most biological treatment experiments are monitored by computing a factor called a loading parameter. This term combines several operating variables which often assists in understanding the observed behavior of biological systems. Several forms for the term exist but one which has proved to be useful in explaining the results of laboratory studies can easily be derived from a statement of mass balance for the system. For a process operating at steady state this balance may be expressed as (Mass in) = (Mass out) + (Mass reacted). Algebraically this expression becomes

$$QC_I = QC_E + \frac{dc}{dt} V \qquad (3)$$

where

Q = volumetric flow in the system,
C_I = influent substrate concentration,

C_E = effluent substrate concentration,
C = substrate concentration in the reactor,
t = residence time in the reactor,
V = volume of the reactor.

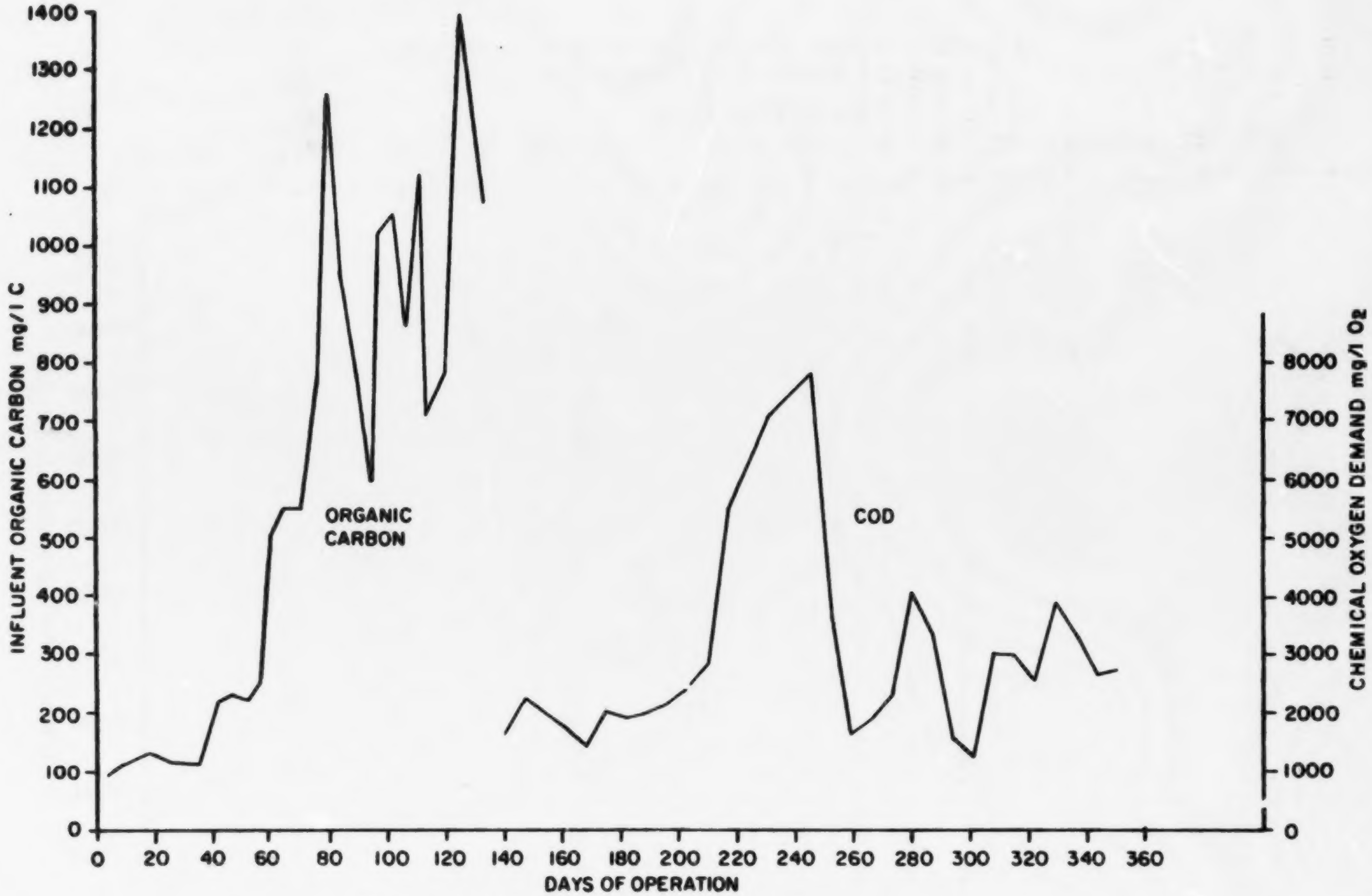

Fig.-6- CARBONACEOUS REMOVAL UNIT
INFLUENT CONCENTRATIONS, ORGANIC CARBON & COD

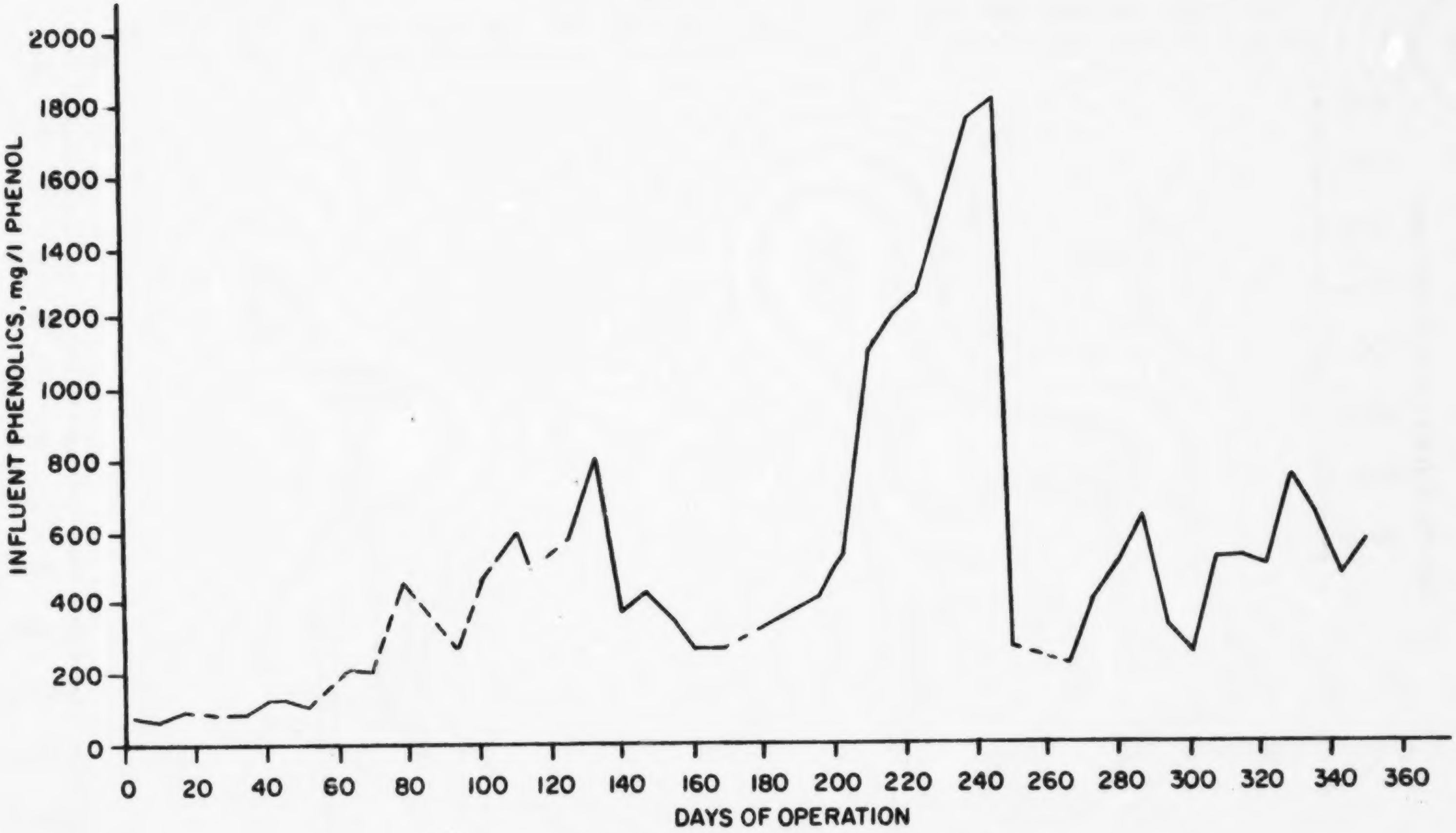

Fig.-7 - CARBONACEOUS REMOVAL UNIT PERCENTAGE CONCENTRATION, PHENOLICS.

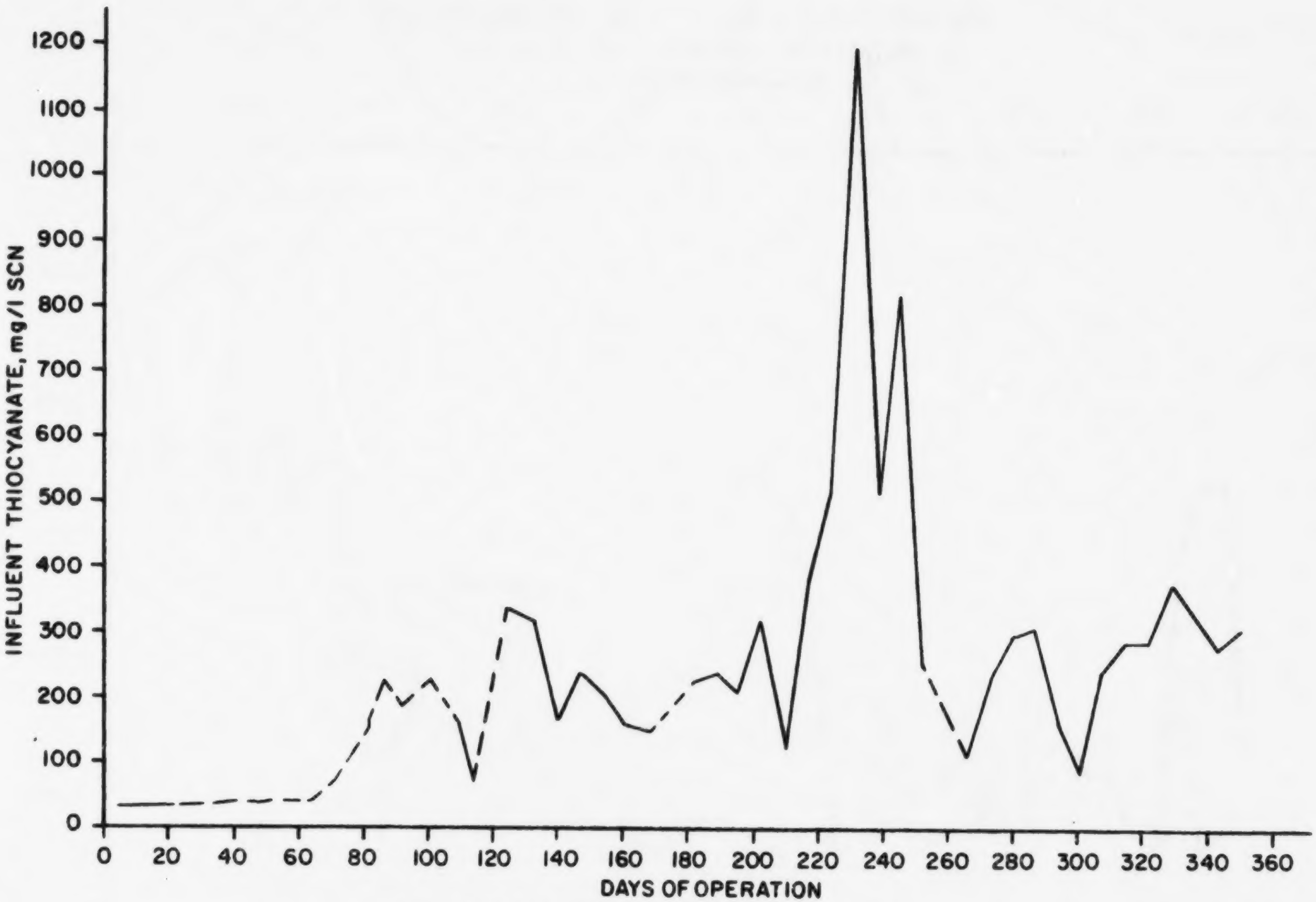

Fig.-8- CARBONACEOUS REMOVAL UNIT
INFLUENT CONCENTRATION THIOCYANATE

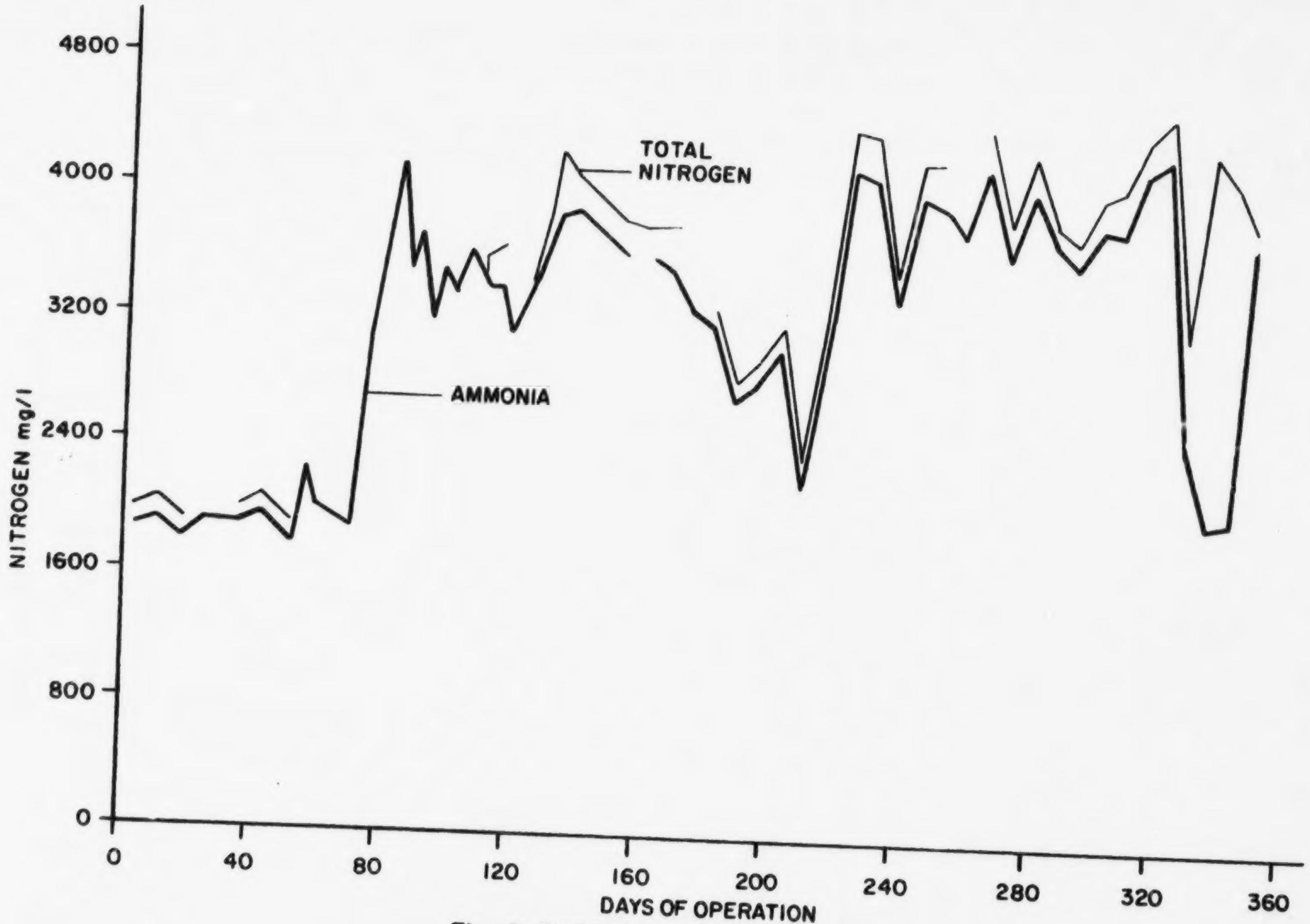

Fig.-9-EXCESS AMMONIACAL LIQUOR CONCENTRATIONS TOTAL NITROGEN AND AMMONIA

For a complete-mix reactor as was used in this study, effluent concentrations equal reactor concentrations ($C = C_E$). In biological systems, the rate of removal of substrate material is known to be proportional to substrate and viable organism concentrations. This may be stated as

$$\frac{dc}{dt} = KCS \qquad (4)$$

where

K = a proportionality constant and
S = viable organism concentration in the reactor.

Substituting equation (4) into equation (3) and reducing yields

$$Q(C_I - C_E) = KCSV \qquad (5)$$

But since $V/Q = t$, the aeration time in the reactor, and $C_I - C_E = C_R$, which is the concentration of substrate removed, equation (5) reduces to

$$\frac{C_R}{St} = KC \qquad (6)$$

The left-hand term of this equation defines the loading parameter. An arithmetic plot of this parameter versus the effluent concentration of substrate should provide a straight line with a slope equal to the proportionality constant K. This derivation assumed constant temperature, proper oxygen tension, appropriate pH levels, satisfactory sedimentation, and, in general, steady state operation. The proportionality constant will vary with all of these and the results of the experiment will be discussed in light of these variables.

In the experimental approach utilized to determine the limiting loading parameter possible in the carbonaceous unit for the various substrates, the system, after proper acclimation, was subjected to increased loadings. System response was measured by monitoring the effluent and viable solids concentration while maintaining a constant aeration time. As loading increases, a point is reached beyond which system failure occurs. This failure may be manifested by an appearance of excessive amounts of substrate or other constituents in the effluent.

A major problem with the use of equation (6) is its failure to signify whether the system is not fully acclimated or is experiencing failure.

For example, in comparison to a system at steady rate, a system not fully acclimated would show a low concentration of substrate removed and a relatively high effluent concentration. After failure, the identical condition exists. This deficiency may be overcome by modification of the equation by converting it to an influent loading factor rather than one based on substrate removal. This modified equation becomes

$$\frac{C_I}{St} = K_m C_E \tag{7}$$

where K_m is a modified constant which may vary slightly with removal efficiency. This equation, although not as theoretically sound as equation (6), does allow prediction of the particular mode in which the unit is operating. The influent loading parameter varies directly with influent concentration. At failure, this term will only reflect changes in the concentration of viable solids in the reactor while the concentration of substrate in the effluent will increase rapidly.

Values for this loading parameter are calculated and given in Table 9 for organic carbon, chemical oxygen demand, phenolics, cyanide, and thiocyanate. These loadings are based on the influent concentrations of each constituent as computed and given in Table 8. The reactor or aeration time is constant for the entire experiment and is one (1) day. The viable solids concentration in the reactor is taken as proportional to the result of the Imhoff cone reading on the mixed liquor. This assumption may be questioned on several points since the Imhoff cone technique measures the volume of settleable solids and as such necessarily is influenced by the settleability of the solids and does not differentiate between viable and non-viable solids. However, the advantages of this quick and simple test conducted routinely for process control by the operator proved to be an adequate substitute for more widely accepted measurements of viable solids. The loading parameter calculated using this substitute for organism concentration will be utilized in subsequent paragraphs to explain operational fluctuations.

In addition to the computed loading factor, the status of operation may also be judged by other parameters including quality of the effluent in terms of contaminant concentrations (Table 9), percentage removals of contaminants (Table 9), effluent loads, and by changes in reactor solids concentration (Table 7). The purpose for the treatment of this waste is to reduce the amount of contaminants in the waste discharge. Since waste discharge effect receiving streams on the basis of mass of contaminants dishcarged, the concentration of a constituent multiplied by the volumetric flow rate is important. In the pilot plant, the flow rate was held constant at one (1) gallon per minute so it can be neglected for comparative purposes. However, the plant was operated with a diluted waste and the dilution factor becomes most important in determining the mass discharge for a full-scale treatment plant. For example, treatment of 25 percent waste with an effluent concentration of 10 mg/l of some constituent discharges a larger mass of material than one operating at 75 percent waste and an effluent concentration of 25 mg/l. Tabulations of effluent discharge loads for comparative purposes for organic carbon, chemical oxygen demand, phenolics, cyanide, and thiocyanate are given in Table 10.

The carbonaceous treatment unit experienced during the operational period of some 352 days several upsets or periods of poor operation. Using the parameters and factors just discussed, the periods of smooth operations and problems will be discussed in an attempt to derive guidelines for design and operation of an ammoniacal liquor treatment unit.

The influent to the carbonaceous treatment units, for the first 55 days of operation, was only about 15 percent waste. In addition, the waste for the entire period was weak but was especially so for the first 40 days. This combination of high dilution and weak waste combined to provide a low influent loading. However, initially the concentration of viable solids in the reactor was low so the influent loading parameter was high. This, parameter decreased rapidly as the unit became acclimated. On or about day 40, the strength of the waste in terms of organic carbon and phenolics almost doubled. This was accompanied by a fall in reactor pH resulting from partial nitrification of ammonia within the carbonaceous removal unit. These changes were reflected in a decrease in reactor solids but the unit continued to operate most satisfactorily as measured by percentage removals or mass discharge of phenolics and organic carbon.

The percentage of waste under treatment was increased to approximately 25 percent beginning on day 56. This was reflected by a corresponding increase in influent loads for organic carbon and phenolics. The system was responding well. Unfortunately, on day 64 the reactor temperature was found to be 123° F, far too high for this type of treatment unit. System problems produced poorer percentage removals of organic carbon (93 to 71), presence of phenolics in the effluent (124 mg/l), increases in the amounts of these two constituents discharged, and a sudden decrease in reactor suspended solids. Unit recovery was rapid for both organic carbon and phenolics but required almost two weeks for suspended solids concentrations to increase substantially.

Corresponding to the sudden increase in reactor suspended solids came a period of high influent organic carbon concentrations. The initial part of this period was also accompanied by a reactor temperature increase from about 80 to 85° F (days 82-91). This short period was a time of excellent treatment with waste percentage at about 40 percent, low influent loading parameters for organic carbon and phenolics, removal of over 90 percent of the organic carbon and the best thiocyanate removal (88 percent) experienced during the entire test.

TABLE 10: EFFLUENT LOADS PER UNIT VOLUME OF WASTE

Period	Percent Waste	Mass Discharged, mg/l per unit of waste					Period	Percent Waste	Mass Discharged, mg/l per unit of waste				
		Organic Carbon, C	Chemical Oxygen Demand, O_2	Phenolics, Phenol	Cyanide, CN	Thiocyanate, SCN			Organic Carbon, C	Chemical Oxygen Demand, O_2	Phenolics, Phenol	Cyanide, CN	Thiocyanate, SCN
1-5	13	250		0.8	5	250	151-157	60	90	1200	0.3	14	270
6-13	15	180		1.3	6	260	158-164	54		1300	0.4	7	310
14-21	17	180		1.2	4	150	165-171	49		1300	0.4	8	350
22-29	15	130		2.7	6	230	172-178	72		1400	-	7	-
30-39	15	120		0.7	7	150	179-185	78		1000	0.4	7	240
40-43	16	140		0.6	13	110	186-192	74		900	0.3	7	340
44-48	16	100		-	21	-	193-199	74		1000	0.3	8	300
49-55	15	130		-	13	-	200-206	74		1400	0.4	7	370
56-57	22	110		0	6	55	207-213	86		900	0.2	4	160
58-60	29	120		-	11	-	214-220	71		2600	0.3	6	380
61-67	23	630		54.	7	370	221-227	68		2600	1.5	7	570
68-73	27	170		0.7	4	240	228-234	79		3000	1.5	6	1500
74-76	25	180		-	6	-	235-241	81		2600	14.	8	480
77-81	24	280		0.3	12	230	242-248	75		3700	21.	7	840
82-84	36	180		-	14	-	249-255	40		3900	0.5	9	370
85-88	42	200		0.5	8	270	256-262	17		3600	-	10	3000
89-91	38	170		-	7	-	263-269	23		2700	0.9	9	960
92-95	47	120		2.1	8	47	270-276	43		1800	0.5	11	440
96-98	61	250		-	9	-	277-283	47		2300	1.2	10	620
99-103	64	80		0.2	12	260	284-290	58		2000	7.4	17	530
104-108	57	250		0.4	8	150	291-297	30		2200	1.3	10	470
109-112	70	90		-	14	-	298-304	22		1800	0.5	12	820
113-116	76	60		0.3	26	260	305-311	35		1400	0.3	12	710
117-121	73	120		7.0	7	250	312-318	45		1600	0.4	13	620
122-129	82	160		0.7	9	-	319-325	45		1600	0.2	14	620
130-136	89	300		0.7	8	380	326-332	58		1200	0.5	9	480
137-143	56	70	1700	0.5	9	430	333-339	49		1300	0.4	9	570
144-150	65	40	1200	0.3	8	240	340-346	46		1600	0.7	11	630
							347-352	47		1600	0.4	11	600

This short period was followed by a decrease in reactor temperature by almost 10° F over a period of about one week. This may have accounted for the appearance of phenolics in the effluent (1 mg/l) and a decrease in reactor solids. Concurrently, the waste percentage under treatment rose to about 60 percent which increased loadings on the unit.

The period between days 99 and 116 was characterized by increasing waste percentages being treated (60 to 75), reactor temperatures about 85° F, good reactor dissolved oxygen concentrations, and overall good removals of major constituents. The slow decrease in reactor suspended solids is believed due to the increase in organism activity resulting from increased temperature.

The system for the period 117-121 suddenly showed a phenolics concentration of 5 mg/l which was followed by a decrease in reactor solids during the next few days. No definite reasons for this system failure can be established but certain observations may be significant. Cyanide concentrations in the raw waste, the unit's influent, and in the effluent had been increasing. During the averaging period just prior to that of failure, cyanide concentrations in the reactor had increased from 10 to 20 mg/l. In addition average reactor dissolved oxygen concentrations had decreased from 4.1 to 2.8 mg/l. The most plausible explanation probably involves the presence of cyanide.

The period from 122-136 was characterized by low reactor suspended solids and increasing percentages of waste treated. The maximum percentage treated was 89 percent. These two factors combined to increase the influent loading parameters for organic carbon and phenolics. Unfortunately, on day 136 the reactor-dissolved oxygen concentration was found to be only 0.2 mg/l which is not considered an adequate level for aerobic treatment. Unit failure is indicated by the low percentage removals of chemical oxygen demand and sudden reductions in reactor suspended solids.

Operations during the interval between day 136 and 172 utilized between 50 and 60 percent waste and the waste during this period was moderately weak. The rather low influent loadings along with reactor temperatures of almost 90° F combined to limit the reactor suspended solids to low levels. Overall the interval was marked by excellent removal of phenolics, probably the best sustained removals of cyanides, only fair removal of chemical oxygen demand, but low mass discharge of COD.

Percent waste being treated was increased on day 172 from about 50 to 75 and was held at this level for about 75 days. The first half of this period was characterized by slowly increasing influent loads of chemical oxygen demand and phenolics. Unit operation was comparatively steady up until day 214 with temperature suspended solids at satisfactory levels. Only occasional marginal dissolved oxygen concentrations were noted and these apparently caused no major operational problems. During this period, the unit treated its highest waste concentration in which reactor foaming was easily controlled. Removals of phenolics were excellent with removals of COD and cyanide of about 60 and 70 percent, respectively. Little or no removal of thiocyanate was experienced which was especially disappointing.

On or soon after day 214 the strength of the raw waste in terms of chemical oxygen demand, phenolics, and thiocyanate suddenly increased by factors of 1-1/2 to almost 4. With essentially a constant percentage of waste in the feed, the unit was subjected to a rather large change in loading. However, the unit continued to remove both COD and phenolics although foaming in the reactor became a problem. From the data, it appears that the unit could have survived this shock loading. Unfortunately, however, the unit in the succeeding weeks was subjected to ever-increasing loads and on at least day 223 to low dissolved oxygen levels and on one day (228) reactor thiocyanate reached 1220 mg/l. The units suspended solids concentrations and its removal of chemical oxygen demand were satisfactory. Actually, only foaming and effluent phenolics concentrations of about 1 mg/l gave indications of problems. A decrease in average reactor temperature from 90 to 78° F over the periods from days 228 to 248 caused major problems including loss of reactor solids and excessive effluent phenolic concentrations.

After unit failure, on day 249, the percentage of influent in the waste was decreased in an attempt to restore performance. Both phenolics and chemical oxygen demand removals improved and from an effluent load viewpoint the unit performed well. The decrease in waste feed percentage was accompanied by a decrease in the raw ammoniacal liquor concentration of phenolics from over 2000 mg/l to 650 mg/l and although a corresponding decrease in COD did not occur immediately, a trend to lower COD levels in the raw liquor was established. Reactor temperatures continued to be low (minimum recorded was 61° F, day 289) until about day 300. The most notable problem during this period was the inability of the unit to accumulate organisms. Treatment efficiency, as measured by effluent quality and mass discharge for phenolics and COD were good. The unit apparently was acting essentially as an aerated lagoon. The major differences between a complete-mix activated sludge system and an aerated lagoon is that in the lagoon no suspended solids are separated from the effluent and returned to the reactor. During this period, this unit operated on this basis since little difference is noted in the concentrations of solids in the mixed liquor and return sludge. In other words, the return sludge was the same as the mixed liquor. This indicates a diffuse growth which settled poorly and contributed to turbid effluent as indicated by relatively low Seechi disk readings during the period. This turbidity also contributed to the effluent COD. This ability of the system to operate insofar as COD and phenolics are concerned as an aerated lagoon under the adverse conditions of low temperature and at only a detention time of 24 hours is most remarkable and should be pursued further.

Attempts to reconvert the system to an activated sludge regime included reseeding of the system about day 260 without success and increasing the reactor temperature around day 300. This latter effort along with a decision to operate the unit at a steady waste feed concentration of 50 percent brought about an almost immediate increase in reactor solids and in sludge returned. Phenolics removal continued to be good and some improvement in COD is noted, at least part of which is due to a less turbid effluent.

In summary the carbonaceous removal unit performed well during much of the test period. Several unfortunate occurrences upset operation but much was learned from these disturbances. Table 11 summarizes the operational parameters and results during those periods of selectively stable operation. Treatment of up to 75 percent raw ammoniacal liquor was demonstrated in a plant operating with an aeration period of 24 hours at temperatures from 75 to 90° F. Influent concentrations or organic carbon, chemical oxygen demand, phenolics, and thiocyanate vary considerably from period to period and do not vary in direct proportion to the percentage of waste under treatment. This indicates the variability in the raw waste under treatment.

Two interesting points concerning the loading parameter are worthy of note. First, levels of 4 to 5 for the organic carbon factor at reactor temperatures of 80 to 85° F appear to be easily treated as judged by percentage removals or organic carbon and phenolics as well as low mass discharges for these constituents. Neglecting the period between 249 and 304, the influent loading parameter for chemical oxygen demand appears to be inversely related to the percent removal of COD. Phenolics loading parameters of around five did not cause problems. The second point of interest is the period between 245-304 when comparatively large values for loading parameters were encountered but reasonably good treatment was attained. This apparently occurred when the unit, probably because of lower operating temperatures, began producing a diffuse biological growth which did not settle. The unit effectively became an aerated lagoon. During this interval the mass discharges of both phenolics and chemical oxygen demand were somewhat greater than when the unit was operating as an activated sludge unit. However, the degree of treatment was surprising considering only a 24-hour aeration time.

The removal of thiocyanate was most discouraging throughout the test. The percentage removal of this constituent seems to decrease as influent waste strength increases. From some recent laboratory work, indications that thiocyanate removing organisms are relatively sensitive and are slow growers has been found. Thus, although some suitable organisms were originally present and became partially acclimated, unit upsets and loadings discouraged the development of the thiocyanate organisms. Removals of cyanide ranged from about 50 to 70 percent. The reasons for only partial removal of cyanide are not known but it is hypothesized that the remainder is in a form not amenable to biological oxidation or air stripping such as possibly a metallic complex or organic compound.

Table 12 summarizes the failures which were experienced by the unit, how the failure was recognized, and the possible cause or causes of the failure. In all, five major failures occurred and caused varying degrees of problems including excessive foaming in the reactor; increases in

TABLE 11: SUMMARY OF CONDITIONS DURING PERIODS OF UNIT STABILITY

Period	OPERATING CONDITIONS									OPERATING RESULTS						
	Percent Waste	Temperature, °F	INFLUENT							PERCENT REMOVALS				MASS DISCHARGES(1)		
			Concentrations, mg/1				Loading Parameter(1)									
			Organic Carbon, C	Chemical Oxygen Demand, O2	Phenolics, Phenol	Thiocyanate, SCN	Organic Carbon	Chemical Oxygen Demand	Phenolics	Organic Carbon	Chemical Oxygen Demand	Thiocyanate	Cyanide	Organic Carbon	Chemical Oxygen Demand	Phenolics
22-55	15	80	180	-	100	40	4	-	2	88	-	50	45	120	-	1.0
82-91	40	85	840	-	350	230	5	-	2	92	-	50	55	180	-	0.5
99-116	70	85	930	-	500	150	4	-	3	92	-	30	50	120	-	0.3
137-171	55	90	-	1800	330	180	-	38	7	-	58	30	65	-	1300	0.4
172-213	75	90	-	2200	550	220	-	21	5	-	62	15	70	-	1100	0.3
249-304	35	75	-	2500	370	210	-	650	110	-	65	10	40	-	2500	1.7
312-352	50	90	-	3000	570	310	-	13	3	-	76	10	50	-	1500	0.4

(1) See text for units.

TABLE 12: SUMMARY OF TREATMENT UNIT FAILURES

PERIOD	Manifestations	Possible Causes
61-67	Reduction in % removal, organic carbon Phenolics present in effluent Increase in mass discharges Decrease in reactor suspended solids	High reactor temperature, 123°F, day 64.
89-91	Phenolics present in effluent Decrease in reactor suspended solids	Temperature decrease accompanied by increase in loadings.
117-121	Phenolics present in effluent	High reactor cyanide levels, up to 20 mg/1. Decrease in reactor dissolved oxygen.
130-136	Reduction in % removal, organic carbon Increase, effluent conc., organic carbon Decrease in reactor suspended solids	Low reactor dissolved oxygen. Increase in load.
214-248	Excessive reactor foaming Low,but unsatisfactory levels of phenolics Low concentrations of reactor suspended solids	Large increase in load . High reactor thiocyanate concentrations. Low reactor dissolved oxygen, intermittently. Decrease in reactor temperature.

effluent concentrations and reductions in percent removals of organic carbon, COD, and phenolics; decreases in levels of reactor suspended solids; and increases in mass discharges of COD. These problems were caused by increases and decreases in reactor temperature, sudden or large increases in loadings, low reactor oxygen levels, and possibly high concentrations of cyanide and thiocyanate. In investigating these failures, not one single case of failure resulting from slow increases in loading was obtained. Thus, maximum possible influent loadings were not necessarily attained.

NITRIFICATION UNIT

The major nitrogenous component in excess ammoniacal liquor is ammonia. In addition, there are smaller amounts of combined nitrogen in organic compounds and thiocyanate. As a result of nitrification in the carbonaceous unit varying amounts of nitrite and nitrate may also be present. In addition to discussing the specific nitrogenous species, a term encompassing all measured forms of nitrogen called total nitrogen is used. Essentially, total nitrogen, as used here, includes that present and measured as ammonia, organic nitrogen, cyanide, nitrite, and nitrate. Thiocyanate-nitrogen is not included as a separate item because it is determined as part of the organic nitrogen fraction.

The nitrogenous composition of the excess ammoniacal liquor utilized during the pilot plant study is given in detail in an appendix and summarized in Tables 5 and 6. Figure 9 graphically presents the ammonia and total nitrogen contents of the waste. The total nitrogen curve is not continuous because of insufficient data for all averaging periods for all of the components which are included in this category. As can be seen, the major nitrogenous component by far is ammonia except for two consecutive averaging periods near the end of the experiment. For these periods, total nitrogen was essentially divided equally between ammonia and organic nitrogen. No satisfactory explanation for this anomalous behavior has been found. In addition, note should be made of the sudden and large changes in ammonia and total nitrogen content of the waste. Changes by factors of about two in the concentrations of these constituents apparently occur with some regularity.

Some apparent removals of nitrogenous components and some interconversions between the various nitrogen-containing compounds take place within the carbonaceous removal unit. Activated sludge plants treating municipal sewage remove from 50 to 85 percent of the organic nitrogen fraction and 15 to 75 percent of the total nitrogen. Nitrogen removals take place by many mechanisms which include coagulation and sedimentation of colloids containing nitrogenous components, especially organic nitrogen; volatilization; and, incorporation into cell substance. Interconversions between forms result from the hydrolysis of organic nitrogen compounds to ammonia and the oxidation of ammonia to nitrite and nitrate. If the oxidation of ammonia takes place, then the loss of nitrogen through denitrification is also possible. These same processes are operative in the treatment of ammoniacal liquor in the carbonaceous removal unit. According to the information given in Table 9, removals of ammonia in the unit ranged from 6 to 40 percent and averaged about 19 percent; total nitrogen removal ranged from 3 to 37 percent and averaged about 15 percent. Unfortunately, nitrite was not determined routinely on the effluent from the carbonaceous unit which casts some doubt on the validity of these removals. Further discussion of this point will be given later in this section.

The second stage of the pilot plant operation, the nitrification phase, was started on January 8 and was initially fed ammonium sulfate and phosphoric acid in an attempt to develop a population of nitrifying organisms. On January 29, the system was converted to a continuous feed of one (1) gallon per minute of carbonaceous effluent. This flow rate represented approximately 24 hours of aeration time. On February 1, collection of routine analytical and operational data commenced and the ensuing discussion covers the period subsequent to this time.

The operating conditions for the nitrification unit are given in Table 13 for averaging periods closely corresponding to those used for the carbonaceous unit. Special attention is called to those periods when the unit was receiving carbonaceous unit effluent, artificial ammonium sulfate and water, and when a combination of the two was being treated. The many changes between operating modes were made because of the varying conditions of the carbonaceous units effluent. Most of the changes were precautionary in that this unit was converted to artificial ammonia before major changes in the carbonaceous unit were made. This was done in order to avoid possible upsets in the nitrification unit resulting from sudden changes in the carbonaceous unit's effluent.

The concentration of viable organisms in this unit remained low at all times despite the fact that no sludge was intentionally wasted. This was somewhat expected in view of the slow growth rate characteristics of the organisms and their relatively poor efficiency in converting inorganic carbon compounds to cell bodies. According to the limited data available, mixed liquor suspended solids probably never exceeded 1,000 mg/l. The Imhoff Cone measurements indicate these low levels also. However, comparisons of the Imhoff Cone measurements between the mixed liquor and return sludge point out that the settleability of the sludge was good for most periods. The Seechi Disk measurements also indicate that the effluent was reasonably clear and free of non-settleable solids.

A major factor of importance to autotrophic bacteria such as the nitrifiers is an available source of inorganic carbon. This carbon can be supplied as carbon dioxide, bicarbonate, or carbonate. These forms of carbonic acid are interrelated through the ionization constants for the acid and the pH. In natural waters, the quantities of these constituents can often be estimated through the determination of alkalinity and pH. Computations

TABLE 13: OPERATING CONDITIONS NITRIFICATION UNIT

Period	Influent, Percent		M. L. Suspended Solids mg/1	Temperature, °F	pH	Alkalinity, mg/1 CaCO$_3$	Dissolved Oxygen, mg/1	Imhoff Conc., ml/1		Secchi Disk, inches	Additives per period									Comments
											pounds							ml.		
	Carbonaceous Effluent	Water						Mixed Liquor	Return Sludge		Ammonium Sulfate	Hydrated Lime	Burnt Lime	Limestone	Sodium Carbonate	Sodium Hydroxide		Tributyl Phosphate	Phosphoric Acid	
2-6	100			82	6.9	90		5	8	4				1						
7-14	100			81	7.1	130		6	10	3			7-1/2	11						
15-22	100			81	7.4	150		5	15	4			19	4						
23-30	100			83	6.9	130		9	20	5		6	12		11					
31-40	100			83	7.3	150		9	28	8		14			40					
41-44	100			79	7.3	130		13	28	8		12			2					
45-49	100			82	6.9	120		17	43	10		15		1/2	2					
50-56	100			82	7.2	120		16	44	6		16		1/2	11					
57-58	100			82	7.1	150		21	47	5		6		1						
59-61	100			83	7.0	140		25	66	6		7		1		2				
62-63	100			85	7.4	130		33	57	5						23				
66-69		100		86	6.6	45		26	63	9	48					31		4	300	
70-74	100			90	6.5	50		32	39	9						22		12		
75-77	100			93	7.3	110		22	58	6					5	35		9		
78-82	100			91	7.1	90		28	56	5					10	95		6		
83-85	100			94	7.1	110		24	50	5					4			4		
86-89	100		510	96	7.4	160		24	54	5					7-1/2	122		16		
90-92	100		830	86	7.2	140		25	30	4					8	92				Temp. drop.
93-96	100		540	85	7.9	530		14	25	5					16	61				Alk. increase.
97-99		100	610	90	8.3	520		13			40				12					
100-102		100	310	94	6.8	80		5	13	6	64				10-3/4				100	
103-104	100		420	91	8.2	350		9	17	7					4					
105-107	100		70	88	7.8	240		4	7	5					12					
108-115		100	150	92	6.8	50	3.4	4	8	10	176				32	17				
116-121	100			92	7.8	270	3.1	6	12	4					8					
122-130		100		89	8.0	210	2.6	2	3	7	144				10				1650	
131-137		100		95	7.1	70	2.0	2	4	10	88				20	6			400	
138-144		100		95	6.9	60	3.0	2	6	16	168				14	67			1400	
145-151		100		95	7.3	100	2.9	3	7	20	168				14	92			1400	
152-156		100		95	8.0	180	2.7	3	6	18	120				10				1000	High pH caused
157-158	25	75		95	6.4	25	2.0	4		11	24				4	2			200	by low O_2.
159-165	30	70		96	6.9	40	2.5	3	8	11					14	78				
166-172	35	65		96	6.9	50	2.6	3	11	9					14	52				
173-179	25	75		95	7.8	200	3.0	3	5	5					12					
180-186		100		96	7.5	110	3.3	3	7	9	88				14	9			1300	
187-193		100		95	6.6	40	3.1	3	4	10	80				14				1400	
194-200		100		95	6.7	40	1.7	1	3	18	80				14				1200	
201-207	15	85		96	8.1	220	1.9	1	5	9					12					
208-214					MAJOR FLOW DISRUPTION															
215-221	25	75		93	7.0	70	2.1	4	9	6					14	100				
222-228	25	75		95	7.1	90	2.3	4	8	6					14	107				
229-235	25	75		95	7.0	90	2.4	9	16	6					12	110		40		
236-242	25	75		90	7.2	100	-	15	25	6					12	100		100		
243-249	25	75		91	6.9	85	2.3	15	26	5					14	77		80		
250-251	25	75		94	6.8	110	2.7	27	60	6					4	35				
252-256	25	75		83	6.7	50	3.1	25	20	7	166				8	63		40		
257-263	25	75		84	6.8	60	2.9	20	40	6	140				14	153		30		
264-270	25	75		89	7.[illegible]	160	3.5	13	16	6	130				14	125				
271-277	25	75		81	7.2	200	4.3	13	20	7	42				14	105				
278-284	25	75		81	7.7	210	4.8	10	10	7	63				14	11				
285-291	25	75		80	7.1	60	3.4	5	8	8	66				14	34				
292-298	25	75		83	6.9	60	2.9	11	7	9	80				14	80				
299-305	25	75		84	6.7	60	3.2	4	8	10	81				14	74				
306-312	25	75	220	87	6.9	60	3.0	4	9	15	84				14	122				
313-319	25	75	340	82	6.8	90	3.1	5	9	10	3				12	97				
320-326	25	75		86	7.3	130	2.9	4	5	10					12	41				
327-333	25	75		82	7.2	90	2.8	5	8	9					14	107				
334-340	25	75		81	7.0	70	2.7	6	15	10					6	90				
341-347	25	75		78	7.4	120	3.0	4	7	6					14	46				
348-352	25	75		88	7.1	70	-	5	7	6					12	38				

based on this simple model would indicate large amounts of inorganic carbon present in the excess ammoniacal liquor. However, in the case of this waste with its large concentration of ammonia and pH values of roughly 8.5-9.0 it can be easily shown that the apparent alkalinity as determined is almost all due to the ammonia and that inorganic carbon levels are relatively low. However, in subsequent treatment stages when ammonia concentrations decrease either through treatment or dilution and the pH decreases, the alkalinity determination does become a measure of the inorganic carbon content. By reference to Appendix A-2, the alkalinity of the carbonaceous units effluent is seen to vary widely. However, if ammonia alkalinity is neglected, the carbonaceous alkalinity is normally only a few hundred parts per million as calcium carbonate. This represents only a small concentration of inorganic carbon. The conclusion is quickly reached that the waste cannot supply the necessary inorganic carbon directly and that this constituent must be supplemented.

A possible source of inorganic carbon would be that produced as consequence of the oxidation of the organic carbonaceous material in the first treatment unit. According to the data in Table 5, the organic carbon content of the raw waste may be as high as 3,000 mg/l. Unfortunately, even though most of this is converted to inorganic carbon, the inorganic carbon is mostly lost as carbon dioxide. To prevent this loss would require pH values in excess of operational limits. However, conservation of inorganic carbon is enhanced by high pH and every effort should be made to operate this unit near the maximum operational pH.

Supplementary inorganic carbon has been required in all laboratory tests as well as in the pilot unit for the nitrification of excess ammoniacal liquor. Sources of inorganic carbon have included limestone, calcium carbonate, and soda ash. Powdered limestone has worked well in the laboratory but only limited experiments were attempted in the field. Sodium carbonate was used almost exclusively because of its effectiveness and ease of handling. The addition of inorganic carbon to an aerated solution such as is encountered in the nitrification unit can lead to loss of the carbon as carbon dioxide depending upon the pH. As the pH decreases from 8, the rate of loss increases. Since the nitrification reaction tends to decrease the pH, control of this parameter is necessary. Several chemicals including hydrated lime, burnt lime, and sodium hydroxide were used for the purpose with sodium hydroxide proving to be most suitable. An attempt to provide a more quantitative view of the alkalinity relationships in the nitrification unit is given in Appendix C.

Phosphoric acid was added to the unit during periods when an artificial feed of water and ammonium sulfate were being treated to supply the biological process with the nutritional necessity, phosphorus. Phosphorus, during treatment of ammoniacal liquor, was present in the effluent from the carbonaceous unit. Tributyl phosphate was occasionally added as an antifoaming agent.

The basic purpose of the nitrification unit is to produce nitrite and nitrate from the incoming nitrogenous constituents. Actually, the true autotrophic nitrifiers are capable only of oxidizing ammonia. However, since no practicable way of limiting the biological activity of the flora in this unit to the autotrophs was available, changes in other nitrogenous constituents is also possible. For these reasons, several approaches to calculating the efficiency of the unit are available and along with the operating results are summarized on Table 14.

Data for four periods are not included because of unsteady operations resulting from changes between carbonaceous effluent feed and artificial ammonia feed in such a way that the changes could not adequately be monitored. In addition, one period was experienced when flow disruptions occurred and the data obtained was not considered representative. The data for periods in which reasonable steady operation was experienced is given.

The first several columns of Table 14 give the nitrogenous components present in the influent to the nitrification unit. These nitrogenous components come from carbonaceous effluent and/or ammonium sulfate. The effluent from carbonaceous unit was monitored for ammonia, organic nitrogen which includes thiocyanate nitrogen, and nitrate nitrogen. The "total" nitrogen listed as being contributed by this source is the sum of these three components and unfortunately does not include nitrite.

When the unit was operating on 100 percent carbonaceous effluent, these concentrations equal those given on Table 9 for the effluent from carbonaceous removal. When, according to Table 13, the unit was treating a diluted carbonaceous effluent the influent nitrogenous concentrations are computed using the appropriate percentage and the analysis of the effluent for that period.

The computation of the concentration of ammonium sulfate in the influent during those periods of its use are based on the flow of water and/or waste and the weights of ammonium sulfate added per period as given on Table 15. Influent total ammonia and total influent nitrogen are the sums of the respective constituents without regard to source. Table 14 also gives a summary of the nitrogenous materials in the effluent from the nitrification unit including ammonia, nitrite, nitrate, total oxidized and a total. In this instance, organic nitrogen determinations were not conducted. As nitrite and nitrate are the designated end products of this unit their concentrations are most important.

The purpose of this unit is to oxidize ammonia to nitrite and nitrate. One way of judging this activity is to observe the amount of ammonia removed. A column for the percent of ammonia removal is given in Table 14. This indicates that removals up to 90 percent were experienced at times but probably something like 60 percent was more common. Since ammonia which passes this phase of treatment unoxidized will not be

TABLE 14

NITRIFICATION UNIT, SUMMARY

PERIOD	Nitrogenous materials, mg/l as nitrogen												Percent Ammonia Removal	Percent of Effluent Nitrogen Oxidized	Total Nitrogen (4)	Percent Nitrogen lost
	Influent							Effluent								
	By source								Oxidized							
	Carbonaceous Effluent															
	Ammonia	Organic Nitrogen	Nitrate Nitrogen	"Total"(2)	Artificial $(NH_4)_2SO_4$	Total Ammonia-N	Total (2) Nitrogen	Ammonia	Nitrite	Nitrate	Total	"Total"(3)				
2-6	200	30	0	230	0	200	230	190	40	40	80	270	5	30	250	-8
7-14	260	30	0	290	0	260	290	220	48	53	100	320	15	31	310	-3
15-22	240	30	0	270	0	240	270	170	56	71	130	300	29	43	330	9
23-30	220	20	1	240	0	220	240	160	61	70	130	290	27	45	-	-
31-40	200	20	70(1)	290	0	200	290(1)	120	77	89	160	280	40	57	290	3
41-44	210	20	90(1)	320	0	210	320(1)	180	69	87	150	330	14	46	330	0
45-49	200	-	60	-	0	200	-	230	69	91	160	390	-	41	310	-26
50-56	230	-	70	-	0	230	-	220	76	108	180	400	-	45	290	-38
57-58	280	20	60	360	0	280	360	220	110	87	200	420	21	48	-	-
59-61	410	-	70	-	0	410	-	310	127	114	240	550	24	44	-	-
62-74			INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS													
75-77	600	-	1	-	0	600	-	190	230	103	330	520	68	64	-	-
78-82	950	50	5	1010	0	950	1010	710	215	182	400	1110	25	36	1300	14
83-85	1220	-	6	-	0	1220	-	610	185	115	300	910	50	33	-	-
86-89	1260	40	5	1310	0	1260	1310	740	344	348	690	1430	41	48	1550	-8
90-92	1190	-	5	-	0	1190	-	550	396	441	840	1390	54	60	-	-
93-96	1290	60	7	1360	0	1290	1360	660	192	214	410	1070	49	38	1560	31
97-122			INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS													
123-130				0	320	320	320	210	3	4	7	220	34	3	320	31
131-137				0	230	230	230	[illegible]	[illegible]	64	130	180	78	72	230	16
138-144				0	430	430	430	[illegible]	[illegible]	145	300	420	72	72	430	2
145-151				0	430	430	430	[illegible]	[illegible]	200	430	480	89	90	430	-11
152-158			INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS													
159-165	500	30	0	530	0	500	530	230	149	112	260	490	54	53	610	20
166-172	540	50	0	590	0	540	590	330	135	138	270	600	39	45	650	8
173-179	520	-	-	-	0	520	-	1000	46	40	90	1090	-	8	-	-
180-186				0	230	230	230	200	25	26	50	250	13	20	230	-9
187-193				0	210	210	210	120	49	37	90	210	43	43	210	0
194-201				0	210	210	210	70	41	37	80	150	67	53	210	29
202-215			FLOW DISRUPTION AND pH PROBLEMS													
216-221	460	30	0	490	0	460	490	190	101	103	200	390	59	51	580	33
222-228	580	40	0	620	0	580	620	330	210	176	390	720	42	54	740	3
229-235	670	40	0	710	0	670	710	380	241	188	430	810	43	53	850	5
236-242	410	20	0	430	0	410	430	250	257	221	480	730	39	66	710	-3
243-249	580	20	0	600	0	580	600	240	227	288	510	750	59	67	780	-4
250-256			INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS													
257-263	130	-	0	-	360	490	-	50	326	366	690	740	90	93	-	-
264-270	190	20	0	210	330	520	540	130	267	335	600	730	75	82	580	-26
271-277	310	20	0	330	110	420	440	150	152	189	340	490	64	69	520	6
278-284	400	20	0	420	160	560	580	510	0	58	60	570	10	10	660	14
285-291	470	20	0	490	170	640	660	400	0	83	80	480	37	17	720	33
292-298	220	20	0	240	210	430	450	110	0	128	130	240	75	54	490	51
299-305	200	20	0	220	210	410	430	70	154	201	350	420	83	83	430	2
306-312	270	10	0	280	220	490	500	110	263	197	460	570	78	81	570	0
313-319	400	10	0	410	10	410	420	80	210	204	410	490	80	84	500	2
320-326	440	10	0	450	0	440	450	190	140	131	270	460	58	59	510	10
327-333	280	100	0	380	0	280	380	50	222	243	460	510	82	90	460	-11
334-340	210	230	0	440	0	210	440	140	209	231	440	580	33	76	530	- 9
341-347	190	230	0	420	0	190	420	360	62	112	170	530	-	32	480	-10
348-352	420	20	0	440	0	420	440	470	127	171	300	770	-	40	450	-70

(1) Includes Nitrite-N.
(2) Does not normally include nitrite
(3) Does not include organic nitrogen.
(4) Influent based on input to carbonaceous unit and percent of effluent fed to nitrification.

TABLE 15: OPERATING CONDITIONS, DENITRIFICATION UNIT

(Influent - constant 1 gpm of nitrification effluent unless noted)

Period	Additives per Period		Temperature, °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l	Imhoff Cone, mg/l		Secchi Disk, inches	Blowdown, %/day	Special Problems				Comments
	Sugar, Pounds	Molasses, liters					Mixed Liquor	Return Sludge			Foaming	Bulking	Influent Flow	Return Sludge	
3-7	20.7	-	79	6.8	140		13	35	5					X	
8-15	15.4	-	77	7.2	230		38	40	4						
16-23	18.4	-	74	6.8	180		29	40	4			X			
24-31	18.4	-	76	7.2	270		23	48	3	2		X	X	X	
32-41	32.6	-	80	7.8	350	2.6	5	7	4	2		X		X	
42-45	16.0	-	79	7.0	300		4	5	5					X	
46-50	20.0	-	76	7.3	370		3	3	3				X	X	
51-57	28.0	-	76	7.0	400		2	3	3						
58-59	8.0	-	77	6.5	440		2	5	2						
60-62	12.0	-	77	7.3	580		6	7	2						
63-75	INTERMITTENT USE OF ARTIFICIAL NO_3 IN UNIT 2														
76-78	-	4.5	87	8.3	360		1	3	4			X		X	
79-83	-	7.5	86	8.0	380		2	4	3					X	
84-86	-	3.5	89	8.0	420		4	8	3						
87-90	-	6.0	89	7.8	290		2	1	3						
91-93	-	4.5	80	7.9	440		0	1	2						
94-97	-	6.0	82	8.5	840		3	3	3						
98-123	INTERMITTENT USE OF ARTIFICIAL NO_3 IN UNIT 2														
124-131	-	24.0	86	7.1	230	-	2	5	2					X	
132-138	-	21.0	91	7.7	390	0.1	1	2	3						Dark color, bad odor.
139-145	-	21.0	92	8.6	470	0.8	1	4	4						
146-152	-	21.0	92	8.7	510	0.1	-	-	4						
153-159	-	21.0	92	8.4	470	0.6	1	2	4						
160-166	-	21.0	92	8.6	520	0.2	0	1	4						
167-173	-	21.0	91	8.4	480	0.2	-	-	-			X			
174-180	-	21.0	91	7.8	390	1.1	1	3	3						
181-187	-	21.0	92	7.2	260	0.0	3	3	3			X	X		
188-194	-	21.0	92	7.8	340	0.0	5	12	4						
195-202	-	24.0	93	7.3	130	0.2	3	1	2						
203-216	MAJOR FLOW PROBLEMS ENCOUNTERED														Intermittent molasses flow.
217-222	-	21.0	93	8.5	670	0.6	2	8	3						
223-229	-	21.0	92	8.5	760	0.0	3	5	3						
230-236	-	21.0	92	8.3	670	0.0	8	15	2			X			
237-243	-	21.0	85	8.5	650	0.0	3	19	2			X			
244-250	-	21.0	88	8.7	731	0.1	3	14	2			X			
251-257	INTERMITTENT USE OF ARTIFICIAL NO_3 IN UNIT 2														
258-264	-	31.5	80	9.2	930	0.1	2	17	2						
265-271	-	31.5	82	9.0	1080	0.1	6	30	3			X			
272-278	-	31.5	76	8.0	685	.8	2	9	3			X			
279-285	-	31.5	78	7.2	350	5.6	1	1	2		X				
286-292	-	27.0	74	7.6	513	0.2	2	24	2		X				
293-299	-	21.0	75	8.5	560	0.5	3	4	3			X			Sludge color reversal.
300-306	-	21.0	82	8.8	620	0.3	2	2	3			X			
307-313	-	28.5	82	9.1	850	0.5	1	3	3			X			
314-320	-	31.5	75	9.3	870	0.3	1	3	3			X	X		
321-327	-	31.5	74	8.1	680	0.3	1	2	3			X		X	Mixed liquor [illegible] 115 mg/l.
328-334	-	31.5	74	9.1	830	0.3	1	2	3			X			
335-341	-	31.5	71	8.7	780	0.3	2	3	3						
342-348	-	27.0	76	7.5	390	0.3	1	1	3						
349-352	-	27.0	80	8.0	600	-	1	3	3		X				

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removed by later stages of treatment, the low percentage obtained limits the overall removal potential for the plant. However, the plant was not operated to produce a consistent effluent because of the many variations in treatment schemes used in both the nitrification and carbonaceous units. Therefore, more normal operation should be expected to approach the maxima rather than the average obtained in such an experiment. Fairly steady operation for the periods near the experiments end possibly indicate that 75 to 80 percent ammonia removal might be anticipated. Another way of looking at the operation of the nitrification unit is to compute the percentage of the effluent nitrogen that is oxidized. According to the column so labeled, values ranging from less than 50 to more than 90 percent were experienced. Since only oxidized nitrogen is capable of removal in the denitrification unit, the percentage oxidized places an automatic upper limit on plant efficiency. Again, values approaching the maxima should be expected under steady plant operations.

Careful scrutiny of Table 14 for the amount of nitrogen in and out of the unit shows that in practically all cases when carbonaceous unit effluent is being used, apparent nitrogen increases occur within the unit. Nitrogen imbalance is expected in biological systems but not in the form of consistent increases. The easiest and most straightforward explanation is to assume that some oxidation of ammonia to nitrite is occurring in the carbonaceous unit. This is partially borne out by the excellent balances obtained for the only periods, 31-40 and 41-44, in which nitrites in the effluent were determined. An additional indication is the frothing noted intermittently in the clarifier of the carbonaceous unit often caused by denitrification. If this is accepted as the explanation, then the apparent nitrogen removals reported for the carbonaceous unit may not be real. In addition, if this is true, then a nitrogen balance across both the carbonaceous and nitrification unit should be of interest. The last two columns of Table 14 provide this information. The total nitrogen here is computed from the influent values of total nitrogen for the carbonaceous unit as given in Table 8 and the percentage of carbonaceous effluent fed to the nitrification unit is given in Table 13. The nitrogen balance in terms of percent lost is inconsistent but varies around zero. This variation around zero is taken as evidence that little or no change in total nitrogen content occurs within the first two treatment units. Thus, the criteria of effluent nitrogen oxidized definitely places the upper limit on the overall plant ability to remove nitrogen either on the basis of percentage or absolute removals. The percentage of effluent nitrogen (roughly equal to plant nitrogen inputs) oxidized has been discussed. This parameter along with the absolute amount of oxidized nitrogen produced will be utilized to define periods of stable and unstable operations.

The first sixty days for the nitrification unit consisted of operating directly on the effluent from the carbonaceous unit. During this period, the carbonaceous unit was treating only a 15 percent dilution of a relatively weak ammoniacal liquor. Operation was not optimum, however, because of low reactor temperature. The response of the nitrification unit to this effluent was slow but steady improvement in the amount of nitrogen oxidized and in the percentage of influent ammonia oxidized. The amount of ammonia removal within the unit remained low and probably indicates that most of the nitrification is taken place within the underloaded carbonaceous unit.

Just as increases in waste loads under treatment were being made, an unfortunate failure of the temperature control equipment for the carbonaceous unit took place and resulted in failure of that unit accompanied by transfer of poorly treated waste to the nitrification unit. This resulted in a drastic decrease in the quantity of nitrogen oxidized by this unit and indicated impending failure. To provide the nitrification unit with an ammonia feed during the interval required for recovery of the carbonaceous unit, intermittent use of synthetic feed was practiced until day 75.

The unit was returned to carbonaceous effluent feed on day 75. This action was accompanied by a change in reactor temperature to about 90°F. During the first week of this interval, the influent ammonia concentration increased from 600 to 1,200 mg/l which represented the maximum concentration of ammonia received by the unit during the entire test. The period between days 82 and 91 was also marked by the excellent treatment of 40 percent waste by the carbonaceous unit. The nitrification unit responded to all these factors by producing rapidly increasing effluent concentrations of oxidized nitrogen. During one sampling interval, effluent oxidized nitrogen increased by almost 150 mg/l per day. This was the maximum observed rate of increase and may give some indication of the response time of the unit to changes in the influent characteristics. Unfortunately, before steady state conditions were established, and just as improving percentages for removal of ammonia, ammonia oxidized, and effluent nitrogen oxidized were becoming apparent, the carbonaceous unit again became upset.

A sudden decrease in the temperature of the carbonaceous unit accompanied by increasing loadings in the periods following day 90 subjected the nitrification unit to a poorer quality effluent including phenolics of about one mg/l for a short interval. In addition, this problem was accompanied by a decrease in nitrification unit temperature (96 to 86°F) and the combination resulted in a sudden decrease in nitrification efficiency. This unit failure was followed by a period from days 97 to 122 of unsteady operation and feed. During this period, the carbonaceous unit again experienced problems and the unit was placed completely on artificial feed. This regime continued from day 123 to 151. With the units temperature around 95°F and pH values ranging from 6.9 to 8.0, the unit responded well with increasing absolute amounts of nitrogen oxidized as well as in percent ammonia removal, ammonia oxidized, and effluent nitrogen oxidized. Close to complete nitrification was experienced during this period.

With the return of the carbonaceous unit to stable operation, the nitrification unit was returned to a treated waste feed about day 155.

The decision was made, however, that the carbonaceous effluent would be diluted prior to being applied to the nitrification unit. The purpose of this dilution was to reduce and dampen fluctuations in the quality of carbonaceous effluent resulting from operational changes in that unit. Unfortunately, three days prior to the conversion (day 152) the nitrification unit, while still on artificial feed, was subjected to a pH of 9.9. Analyses of samples taken the following day indicated a decrease in nitrification. However, before all of the ramifications of the units condition were known, the unit was converted to diluted waste. The unit did not respond and was returned to artificial feed on day 180 without success.

Following a time of treatment disruptions resulting from mechanical problems, the unit was again placed on a feed of diluted carbonaceous effluent on day 216. This time the unit responded slowly and showed a steady improvement in nitrified nitrogen. During this interval reactor temperatures of about 90°F and pH values around 7 were experienced. On day 249, after about two weeks of poor quality carbonaceous effluent, the nitrification unit was placed on intermittent synthetic feed to avoid upsetting this unit. On day 257, after improvement in the carbonaceous unit, the nitrification unit began receiving an effluent supplemented by artificial ammonia. Upon resumption of treatment the unit apparently had no ill effects from the transition. Oxidized nitrogen levels as well as percent ammonia oxidized and effluent nitrogen oxidized were all at or near maximum possible levels.

This period of excellent performance was followed by a period which extended to the end of the experiment in which reactor temperatures were low, mostly in the low to middle eighties. This period can be subdivided into two parts based on influent feed. The first part, from about days 260 to 310 consisted of a diluted carbonaceous effluent plus artificial ammonia. Unit response was not satisfactory. The combination of low reactor temperature plus a relatively poor carbonaceous effluent resulting in high loadings of chemical oxygen demanding materials including phenolics may have been responsible.

The second part of this period, from about day 315 to the experiment's conclusion, utilized only diluted carbonaceous effluent without supplemental ammonia. This effluent was much improved in quality over that of the preceding period. The nitrification unit responded well, especially in light of the low reaction temperature, by providing several short periods in which excellent nitrification occurred and in which 75 to 90 percent of the nitrogen was nitrified.

A major problem with the entire nitrification experiment was that conditions were never stable enough for a period of sufficient length to allow establishment of a steady state. In biological systems, variation almost invariably leads to less than optimum performance. Good nitrification was obtained most consistently only when the carbonaceous unit was operating in a satisfactory manner. In addition, best nitrification was obtained at reactor temperatures of 90 to 95°F with relatively poor nitrification at 80 to 85° F. Unit failures or problems resulted mostly from carbonaceous unit failures. One failure was caused by a high reactor pH 9.9. The optimum pH range appears to be about 6.8 to 8.2.

An attempt to outline a reaction mechanism for the nitrification unit including an alkalinity balance computation is given in Appendix C.

DENITRIFICATION UNIT

Denitrification is the major function of the third treatment stage. As outlined previously in Section V, denitrification is the process in which nitrate and nitrite nitrogen is biochemically reduced to nitrogen gas with the concurrent oxidation of organic matter. Denitrification thus has the potential for converting potential nitrogenous contaminants into an inert form.

The denitrification system was placed on line January 29, 1970, and initially received one (1) gallon per minute of nitrification unit effluent. This flow represented a reaction time of approximately 8 hours. Detailed surveillance of the influent and effluent began with the first averaging period in February which began for this unit on the third because of the two 24-hour detention periods in the preceding treatment stages.

Tables 15 and 16 provide summaries of the operating conditions and operating results for the denitrification unit. More detailed information may be found in the Appendix. Being the last of the three units, the denitrification reactor was subjected to all of the fluctuations either encountered or resulting from the previous treatment stages.

Table 15 gives the summary of the major operational parameters measured routinely during the test of the denitrification unit. Essentially the only control exercised over this unit was through the amount of reducing agent added. During roughly the first one-fifth of the experiment, sucrose sugar was used while in the remainder of the experiment, molasses was used. The amounts of these materials added are given for each period in the first two columns. As with all biological processes, temperature and pH are important, but no control over these parameters was exercised in the denitrification unit. Temperature within the reactor varied from a low of 71 to a high of 93°F. This variation would be expected to influence greatly the rate of denitrification. The pH and alkalinity increase as a result of the overall denitrification process. Values of pH as high as 9.2 and alkalinity increases of up to almost 1,000 mg/l as $CaCO_3$ were experienced. Dissolved oxygen concentrations approaching one mg/l were encountered during the experiment without apparent disruption of denitrification.

The denitrification process depends upon the availability of organisms capable to utilizing oxidized nitrogen in their metabolic processes. The use of the Imhoff Cone to measure the concentration of these organisms in this unit was less than adequate. First, the Imhoff Cone measurement depends upon sedimentation of the organisms and denitrifying sludges, instead of settling, often tend to float because of entrapment of released nitrogen gas. An additional complication resulted because, without doubt, some biological growth took place because oxygen entered the system through the surface of the stirred reactor. Despite these complications, there is some evidence from the data to suggest that Imhoff Cone readings do correlate with the degree of denitrification. Limited suspended solids measurements indicate low biological levels. No routine blowdown from this unit was made. Blowdown actually occurred through the discharge of a turbid effluent resulting from poor sedimentation of this particular sludge. Low Seechi Disk readings confirm the turbid nature of the effluent.

The operational problems encountered by this unit included, in addition to mechanical problems such as influent flow and sludge return disruptions, a bulking sludge on occasion. The bulking nature of the sludge made mandatory a surface skimming device to collect sludge from the sedimentation compartment for return to the reactor.

The major operational function of the denitrification unit is to reduce the nitrite and nitrate formed in the preceding treatment units to nitrogen gas using an added reducing agent. Obviously, the nitrite and nitrate concentrations in the influent and effluent are important operational parameters and are tabulated in Table 16. Since one of the functions of the three-stage plant was the overall removal of nitrogenous matter, ammonia and total nitrogen concentrations are also given.

The organic content of the effluent is a most important operational factor. The origin of this material may be either the residual not removed in the two preceding treatment units or that intentionally added as either sugar or molasses. These quantities are entered in Table 16 in terms of chemical oxygen demand. To assist in judging the efficiency of the treatment unit, percent losses or removals of ammonia, oxidized nitrogen, total nitrogen, and chemical oxygen demand are also listed.

The removal of ammonia is not a function of this unit and losses of this component were not expected to be large. Small losses may be accounted for by incorporation into the sludge. Actually, as can be seen from Table 16, in many of the periods ammonia increases within the unit are noted. Since ammonia removal is one of the primary objectives of the treatment scheme, any increase in ammonia is undesirable. Several possible reasons exist for this observation. The worst possible case would be the reconversion of nitrite and nitrate by denitrification into ammonia rather than nitrogen gas and organisms are known which are capable of this. Unfortunately, if this were the case, nothing would be accomplished by the nitrification and denitrification treatment steps.

The non-consistent nature of the gains and losses in ammonia cast some doubt on this explanation. More careful examination of the operating conditions existing during periods of gains and losses of ammonia pointed out an interesting correlation. With only a very few exceptions, ammonia gains are noted only when artificial ammonia is being added to the nitrification unit and only losses occur when the nitrification unit is entirely on waste feed. The best explanation for this observation appears to be purely an operational one rather than biological. During times of artificial ammonia additions to the nitrification unit, slugs of ammonia sulfate were added once per day. This meant that ammonia concentration in the effluent varied with time. In addition, the amount in the effluent from the denitrification unit would also vary. Since samples for ammonia were collected simply by grab techniques, the observed results could easily be obtained. However, when all units are treating waste waters, there is no slug effect as all systems are running smoothly and concentrations of constituents do not change rapidly. At any rate, during periods when waste is being treated and since this is the time of maximum importance, small losses of ammonia, possibly ranging to 10 or 20 percent, might be expected within the denitrification stage.

The major change expected within this unit is the decrease in the content of oxidized nitrogen. Oxidized nitrogen losses of greater than 95 percent occurred with some regularity during the test. Considering the lack of consistency in the preceding treatment steps, these results indicate that the denitrification unit is capable of performing its intended function.

The loss of total nitrogen in the unit is not an effective measure of the efficiency of the denitrification treatment unit alone, but rather of the nitrification and denitrification unit combined. For the most part, only the nitrification unit can treat ammonia and the only nitrogenous materials capable of sizable removals in the denitrification unit are oxidized forms. Thus, only with both units operating at peak efficiency will good overall removals of nitrogen be obtained. Unfortunately, the nitrification unit seldom oxidized more than 75 percent of its effluent nitrogen. This means that for most of the time at least 25 percent of the nitrogen passing on to the denitrification unit was unoxidized. For practical purposes, 75 percent removal of total nitrogen is an upper limit even with 100 percent effectiveness of the denitrification stage. Actual losses approaching 70 percent were measured for some averaging periods.

The reduction of oxidized nitrogen by the use of artificial reductants such as sugar or molasses needs careful control. Only with control can the proper stoichiometric quantity be added that will supply just enough reductant to reduce the oxidized nitrogen content adequately without providing an excess that will not be oxidized and thus pass

TABLE 1[illegible]: OPERATING RESULTS, DENITRIFICATION UNIT

PERIOD	INFLUENT CONCENTRATIONS, mg/l								EFFLUENT CONCENTRATIONS, mg/l						LOSSES, PERCENT				
						COD, as O_2												COD	
	Ammonia-N	Nitrite-N	Nitrate-N	Total Oxidized Nitrogen-N	"Total"(1) nitrogen-N	Nitrification Effluent	Increment Added	Total	Ammonia-N	Nitrite-N	Nitrate-N	Total Oxidized Nitrogen-N	Total Nitrogen-N	COD as O_2	Ammonia	Oxidized Nitrogen	Total Nitrogen	Total	Increment Added
3-7	190	40	40	80	270		380	-	170	23	24	50	270		10	37	0		
8-15	220	48	53	100	320		210	-	210	2	2	5	240		4	95	33		
16-23	170	56	71	130	300		210	-	170	33	40	70	270		0	46	10		
24-31	160	61	70	130	290		210	-	140	8	11	20	180		12	91	38		
32-41	120	77	89	160	280		300	-	100	17	20	40	160		16	75	43		
42-45	180	69	87	150	330		380	-	150	0	1	1	190		16	99	42		
46-50	230	69	91	160	390		380	-	170	0	1	1	-		26	99	-		
51-57	220	76	108	180	400		380	-	210	0	2	2	240		4	98	40		
58-59	220	110	87	200	420		380	-	180	0	1	1	210		18	99	50		
60-62	310	127	114	240	550		380	-	290	0	1	1	-		6	100	-		
63-75	INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS																		
76-78	190	230	103	330	520		330	-	140	11	82	90	-		26	73	-		
79-83	710	215	182	400	1110		330	-	630	130	110	240	900		11	40	19		
84-86	610	185	115	300	910		260	-	980	92	58	150	1190		neg.(2)	50	neg.		
87-90	740	344	348	690	1430		330	-	740	260	260	520	-		0	25	-		
91-93	550	396	441	840	1390		330	-	530	410	330	740	1330		3	12	4		
94-97	660	192	214	410	1070		330	-	890	190	200	390	-		neg.	5	-		
98-123	INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS																		
124-131	210	3	4	7	220		660	-	410	0	0	0	420		neg.	-	neg.		
132-138	50	67	64	130	180		660	-	140	13	17	30	170		neg.	77	5		
139-145	120	156	145	300	420	220	660	880	180	21	69	90	290	460	neg.	70	31	61	82
146-152	50	230	200	430	480	300	660	960	110	100	91	190	320	420	neg.	56	33	56	82
153-159	INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS																		
160-166	230	149	112	260	490	340	660	1000	200	14	15	30	260	440	13	89	48	56	82
167-173	330	135	138	270	600	350	660	1010	310	8	6	16	350	440	6	96	42	57	86
174-180	1000	46	40	90	1090	490	660	1150	460	0	0	0	-	950	4	100	-	17	30
181-187	200	75	26	50	250	90	660	750	360	0	0	0	380	740	neg.	100	neg.	0	2
188-194	120	49	37	90	210	80	660	740	170	0	0	0	190	310	neg.	100	10	58	65
195-202	70	41	37	80	150	80	660	740	110	13		30	150	330	neg.	60	0	55	62
203-216	MAJOR FLOW PROBLEMS ENCOUNTERED																		
217-222	190	101	103	200	390	400	660	1060	150	12	10	22	200	550	21	89	49	48	77
223-229	330	210	176	390	720	570	660	1230	300	7	6	10	350	630	9	97	51	49	91
230-236	380	241	188	430	810	650	660	1310	370	31	25	60	600	850	2	86	16	35	70
237-243	250	257	221	480	730	620	660	1280	250	70	74	140	440	660	0	70	40	48	94
244-250	240	227	288	510	750	650	660	1310	170	70	103	170	720	800	29	67	4	39	77
251-257	INTERMITTENT USE OF ARTIFICIAL AMMONIA ADDITIONS																		
258-264	50	326	366	690	740	510	1000	1510	90	86	105	190	-	960	neg.	72	-	37	55
265-271	130	267	335	600	730	500	1000	1500	170	3	7	10	230	910	neg.	99	68	40	59
272-278	150	152	189	340	490	430	1000	1430	140	18	16	30	270	1020	6	91	45	29	41
279-285	510	0	58	60	570	280	1000	1280	530	0	0	0	580	1070	neg.	100	0	16	21
286-292	400	0	83	80	480	300	850	1350	470	0	0	0	490	1020	neg.	100	0	24	39
293-299	110	0	128	130	240	360	660	1020	150	0	29	30	220	640	neg.	78	10	37	58
300-306	70	154	201	350	420	430	660	1090	100	38	32	70	200	500	neg.	80	52	54	89
307-313	110	263	197	460	570	420	900	1320	130	29	32	60	230	580	neg.	87	60	56	82
314-320	80	210	204	410	490	440	1000	1440	80	19	15	30	150	580	0	93	70	60	86
321-327	190	140	131	270	460	360	1000	1360	160	0	0	0	210	730	16	100	54	46	63
328-334	50	222	243	460	510	450	1000	1450	50	26	27	50	180	630	0	89	65	58	82
335-341	140	209	231	440	580	470	1000	1470	130	26	31	60	340	690	7	87	41	53	78
342-348	360	62	112	170	530	360	850	1210	470	1	2	3	510	670	neg.	98	4	45	64
349-352	470	127	171	300	770	340	1000	1340	460	0	0	0	490	660	2	100	36	51	88

(1) Does not include organic nitrogen.

(2) Negative loss, a gain.

through the plant and degrade effluent quality. Reductants, as measured by the chemical oxygen demand and mentioned previously, are either residual organics resisting removal in the previous treatment steps or artificial additions of sugar or molasses. The losses or utilization of the total chemical oxygen demand is given as a percentage of total input to the system in Table 16. These values for the most part vary between 40 and 60 percent. The removals are low in part, because of the refractory nature of much of the COD. The utilization of added COD materials which are not refractory is given in the last column. Percentage losses for COD on this basis approaches 90 percent in some tests.

The most critical aspect of the operation of the denitrification unit is the determination of the amount of reductant necessary to result in removal of the oxidized nitrogen without having an excess. This amount of reductant can be estimated in several ways. Stoichiometrically, the amount can be computed based upon assumed oxidation-reduction reactions and measured concentrations of nitrite and nitrate. These computations for the last three months of the test are given in Table 17. The concentrations of oxidants, nitrite and nitrate and reductants as measured by chemical oxygen demand both in and out of the unit are reproduced from Table 16. The following derivations allow the conversion from concentration units to milliequivalents per liter (meq/l):

(1) Nitrite to nitrogen gas

$$2NO_2^- + 8H^+ + 6e \longrightarrow N_2 + 4H_2O$$

Thus,

$$\text{meq/l } (NO_2^-) = \frac{3}{14} C_{NO_2^-}$$

where the electron (e^-) change per mole or equivalents per mole of nitrite equals 3 and there are 14 grams of nitrite-nitrogen per gram molecule. C_{NO_2} - is the concentration of nitrite in mg/l as nitrogen.

(2) Nitrate to nitrogen gas

$$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$$

Thus

$$\text{meq/l } (NO_3^-) = \frac{5}{14} C_{NO_3^-}$$

TABLE 17: DENITRIFICATION - STOICHIOMETRIC COMPUTATION

Period	OXIDANTS									REDUCTANTS				Error	
	Nitrite				Nitrate				Total Change meq/1	Chemical Oxygen Demand					
	In	Out	Change		In	Out	Change			In	Out	Change		Ox.-Red.	% of Reductants
	mg/1	mg/1	mg/1	meq/1	mg/1	mg/1	mg/1	meq/1		mg/1	mg/1	mg/1	meq/1	meq/1	
279-285	0	0	0	0	58	0	58	21	21	1280	1070	210	26	- 5	19
286-292	0	0	0	0	83	0	83	30	30	1350	1020	330	41	-11	27
293-299	0	0	0	0	128	29	99	35	35	1020	640	380	48	-13	27
300-306	154	38	116	25	201	32	169	60	85	1090	500	590	74	11	15
307-313	263	29	234	50	197	32	165	59	109	1320	580	740	93	16	17
314-320	210	19	191	41	204	15	189	68	109	1440	580	860	108	1	1
321-327	140	0	140	30	131	0	131	47	77	1360	730	630	79	- 2	3
328-334	222	26	196	42	243	27	216	77	119	1450	630	820	102	17	17
335-341	209	26	183	39	231	31	200	71	110	1470	690	780	98	12	12
342-348	62	1	61	13	112	2	110	39	52	1210	670	540	68	-16	24
349-352	127	0	127	27	171	0	171	61	88	1340	660	680	85	3	4

(3) Chemical Oxygen demand

The COD reaction in terms of oxygen can be written as

$$2O^{-2} \longrightarrow O_2 + 4e^-$$

Thus,

$$\text{meq/l (COD)} = \frac{1}{8} C_{COD}$$

Using these equations, the change in milliequivalents per liter of nitrite, nitrate, and chemical oxygen demand between the influent and effluent of the unit were computed. Since, on an equivalent basis, oxidations must equal reductions, the difference or error should be zero. Actual errors, for those averaging periods shown in Table 17, are as high as 17 meq/l and up to almost 30 percent. Computations of the same parameters for less uniform operating periods show even larger errors. The fact that the computed errors show excesses of oxidants during some periods and almost equal excesses of reductants during others tends to indicate that no consistent error was incorporated into the reaction theory. In other words, the reactions proposed fit the experimental data as well as could be expected. The errors may well result simply from the unsteady nature of the operation and the use of grab samples. In addition, the changing efficiencies in the separation of the organisms in the sedimentation tank due to sludge bulking and other factors can have a large effect on the chemical oxygen demand of the effluent and in turn on the redox balance.

All in all, the theory proposed agrees with that found in the laboratory experiments and that proposed by others, and this data tends to varify its validity. On this basis, it is assumed that the major reduction reactions occurring within the denitrification unit are the formation of nitrogen gas from nitrite and nitrate and that the simultaneous oxidation involves converting organic carbon to carbon dioxide. The latter reaction can be monitored easily through the use of chemical oxygen demand measurements. The dosage of organic reducing agent needed for denitrification can then be computed in terms of COD for various nitrite and nitrate concentrations by the following equation:

$$D_{COD} = 8\left(\frac{3}{14} C_{NO_2^-} + \frac{5}{14} C_{NO_3^-}\right)$$

where D_{COD} = stoichiometric COD dosage in mg/l,

$C_{NO_2^-}$ = nitrite concentration in mg/l as N, and

$C_{NO_3^-}$ = nitrate concentration in mg/l as N.

This stoichiometric computation may be used as a first approximation of the required amount of reducing agent to convert the oxidized nitrogen forms to nitrogen gas. However, this computation assumes that the reaction will go to completion without excess reagent being present. Data, as given on Table 16, indicates that during the best period of operation, 91 percent of the added chemical oxygen demand was oxidized while 97 percent of the oxidized nitrogen was lost.

Several other tests indicate that 90 percent of COD and 95 percent loss of nitrogen should be possible with proper analytical and operational controls. The total amount of COD necessary in terms of mg/l, T_{COD}, then would equal

$$T_{COD} = 8.9 \left(\frac{3}{14} C_{NO_2^-} + \frac{5}{14} C_{NO_3^-}\right)$$

The concentration of COD in the effluent would be the residual passing through the nitrification unit plus an amount approximately equal to 10 percent of T_{COD}. The effluent would also be expected to contain about 5 percent of the oxidized nitrogen in the influent to the denitrification unit.

SECTION IX

SPECIAL STUDIES

During the course of this investigation, several special projects were conducted to enhance the understanding of ammoniacal liquor treatment, to extend treatment capabilities, to investigate use of supplementary treatment steps, and to reduce treatment costs. These studies of most interest were concerned with the carbonaceous treatment unit and development of alternate methods of denitrification.

CARBONACEOUS UNIT

The treatment of ammoniacal liquors for removal of carbonaceous materials has been repeatedly demonstrated. However, the treatment has only been accomplished with considerable difficulty and with less than optimum results in some instances. For example, the waste must be diluted prior to treatment and thiocyanate has been difficult to remove.

Near the end of the experimental phase of this project, a pretreatment step was proposed that reportedly made the waste more amenable to biological treatment. This proposal was made by International Hydronics Corporation, and reference is made to this under the authors' names, W. G. Cousins and A. B. Mindler, in Section V. Essentially this pretreatment process consists of free and fixed ammonia distillation at pH 11, followed by addition of spent pickle liquor for both neutralization and coagulation. Following sedimentation, the waste is reported to be more easily treated.

The laboratory modification of the proposed pretreatment step was to treat a batch of excess ammoniacal liquor with lime to a pH of 11 and to heat this mixture to approximately 93°C. Aeration was then applied to strip ammonia to any desired level. After cooling, synthetic spent pickle liquor consisting of one percent free hydrochloric acid and 6 percent ferrous iron was added to chemically coagulate the liquor and to reduce the pH of the waste to about 9. After sedimentation, the waste was ready for treatment in the experimental unit. Typical percentage reductions in some of the major components as a result of the treatment are given in Table 18 for an excess ammoniacal liquor from a coke plant in the Pittsburgh, Pennsylvania, area. As can be seen, this treatment procedure results in a considerable change in some of the major waste constituents, especially cyanide.

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TABLE 18: PRETREATMENT OF EXCESS AMMONIACAL LIQUOR, PERCENT REMOVALS

Constituent	Aeration only	Coagulation only, no aeration	Aeration and coagulation
Chemical oxygen	25	20	30
Thiosulfate	25	20	35
Sulfide	20	10	30
Organic carbon	20	10	25
Phenolics	15	10	20
Ammonia	--	0	--
Cyanide	80	90	90
Thiocyanate	0	0	0

The treatability of this waste without pretreatment, with full pretreatment, and with coagulation alone, have been compared on a laboratory scale. The test procedure utilized the complete-mix activated sludge process operated with a 24-hour aeration time at room temperature. Under these conditions, the waste with no pretreatment could be treated only at less than a waste concentration of 60 percent. With pretreatment, either with or without ammonia removal, the waste was easily treated without dilution. Typical results for the treatment of pretreated wastes are given in Table 19. These results indicate that little or no difference exists between the results obtained with the two levels of pretreatment. It should be noted that the waste was treatable at levels of ammonia-nitrogen of over 4,000 mg/l which is over 4800 mg/l as ammonia. This tends to refute those who have proposed treatment inhibition at levels above 2000-4000 mg/l of ammonia.

TABLE 19: BIOLOGICAL REMOVALS FROM PRETREATED WASTE

Constituent	Pretreatment Procedure					
	Aeration & Coagulation			Coagulation only		
	Conc., mg/l		percent	Conc., mg/l		Percent
	Inf.	Eff.	Removal	Inf.	Eff.	Removal
Ammonia, N.	500	-	-	4000	-	-
Phenolics, phenol	1700	2	99+	1400	3	99+
Organic carbon, C	2000	700	65	1900	800	60
Thiocyanate, SCN	960	920	5	1100	1100	0
Chemical oxygen demand, O_2	7100	2800	60	6800	2900	55

The difference between the treatability of pretreated waste and that of untreated waste does show the inhibitory effect of some one or more components of the waste removed by the pretreatment step. No attempts were made to define more closely the limiting parameter with regard to treatability. A definite factor to be weighed in relationship to increased treatability with this particular pretreatment process is the disposal of the large amount of sludge produced in the liming and coagulation steps.

The removal of thiocyanate, both in the laboratory and the pilot-plant phases of this project has been less than anticipated. A decision was made to attempt to find the operating parameters necessary for the biological oxidation of thiocyanate. The problem with previous experiments and the pilot plant was that the operational parameters on which treatment efficiency was based were phenolics, organic carbon or chemical oxygen demand. The operational parameter for the new test unit would include thiocyanate removal. The design of this special series of tests incorporated many of the concepts on ammoniacal liquor proposed by Ashmore, et al. and outlined in Section V.

The first attempt to obtain thiocyanate oxidation was to reduce the loading on an existing laboratory activated sludge unit. This trial was totally unsuccessful. Next, an entirely new complete-mix activated sludge unit was established specifically for thiocyanate. New seed organisms for this unit were obtained from a sewage treatment plant in Pittsburgh, Pennsylvania, area. Excess ammoniacal liquor was obtained from a coke plant in the same area. The initial influent to this unit consisted of a 10 percent dilution of excess ammoniacal liquor whose pH had been adjusted to about 7 and to which phosphate had been added. At this dilution, the influent contained about 140 mg/l of phenolics and 105 mg/l of thiocyanate.

Operating with an aeration time of 24 hours, after five days over 90 percent removal of phenolics was noted but no thiocyanate was removed. Under past operating criteria, waste strength would have been increased based on phenolics removal; but since in this instance thiocyanate removal was paramount, influent loading was maintained. It was not until day 12 that thiocyanate removal was noted. On that day, about 50 percent removal was noted, and on the following day over 99 percent was lost. The influent waste concentration was then slowly increased in steps with careful monitoring of the effluent for phenolics and thiocyanate. After each incremental increase, both phenolics and thiocyanate would normally be present in the effluent in low concentrations with phenolics disappearing before the thiocyanate. After a few failures of the system, it was determined that with this particular ammoniacal liquor, only about 25 percent waste could be treated in the test unit and obtain consistent removals of thiocyanate of better than 90 percent. The maximum concentration of thiocyanate treated under these conditions was about 300 mg/l with effluent levels of about 10 mg/l.

After the conclusion was drawn that the limiting concentration of this excess ammoniacal liquor that could be processed in the test unit for thiocyanate removal was 25 percent, the unit was converted to coagulated waste feed. The use of pretreated waste allowed the use of 50 percent waste concentrations to be utilized by the unit, and to maintain thiocyanate removals. Thiocyanate levels as high as 525 mg/l were reduced to 20 mg/l during periods of optimum operations.

In summary, for laboratory units utilizing a 24-hour aeration time and room temperatures, treatment for phenolics removal was possible at a maximum waste concentration of 60 percent. This waste, with pretreatment, could be treated for phenolics removal without dilution. Thiocyanate removal from this same waste was only possible at a waste concentration of 25 percent and with pretreatment, this maximum was increased to 50 percent.

Chemical studies of the reaction products of the thiocyanate sulfur indicates that about one-half is converted to sulfate with no sulfide, sulfite, or thiosulfate. The exact fate of the other half was not determined but elemental sulfur is suspected.

DENITRIFICATION UNIT

Sizeable quantities of reducing agent are needed to satisfy the demands of a well-nitrified ammoniacal liquor in the denitrification process. The use of either sugar or molasses for this purpose is expensive and alternatives were sought. Among the alternatives given consideration were the use of ferrous iron, the raw waste itself, and municipal sewage.

The use of ferrous iron, a well-known chemical reducing agent, for the treatment of coke plant wastes appears to be an optimum solution considering that the steel industry also produces sizeable quantities of wastes containing ferrous iron. A report by Gunderloy, et al. (65) proposes the use of ferrous iron specifically for denitrification. Numerous attempts by the laboratory staff to reproduce the results reported or to denitrify wastes were unsuccessful as most all of the oxidized nitrogen reduced could be accounted for as nitrite or ammonia. After considerable testing, this alternative was abandoned.

Another potential alternative for a source of reducing agent was the waste itself. The wastes capacity for reduction is measured by its chemical oxygen demand. Several operational schemes are possible in which great savings in air requirements and neutralizing chemicals can accrue it raw waste can be treated using nitrite and nitrate as oxidizing agents. Unfortunately, denitrification could not be initiated using ammoniacal liquor as the reductant even though much care and patience was exercised.

A last possibility considered was the use of the nitrified effluent from the second stage of the treatment scheme to oxidize or treat municipal wastes. Many (see Section V) have shown that oxidized nitrogen can be used as a substitute for some of the oxygen required to satisfy the carbonaceous oxygen demand of domestic wastes. As an example of the potential of this process, let it be assumed that the excess ammoniacal liquor has an ammonia concentration of 4000 mg/l. In addition, assume that one-half of the ammonia is nitrified to nitrite and the other to nitrate. According to equations developed in Section VIII, this amount of nitrite and nitrate will equal about 1150 milliequivalents per liter for the reaction to nitrogen gas. The non-settleable chemical oxygen demand of a municipal waste is estimated to be about 200 mg/l. In terms of milliequivalents per liter, this is 25. This means that for a stoichiometric reaction the flow of municipal waste would need to be almost 50 times the flow of ammoniacal liquor. In other words, 100,000 gallons of a well-nitrified ammoniacal liquor could satisfy the entire carbonaceous oxygen demand of 5 million gallons of domestic sewage. The savings in denitrification cost to the coke plant and aeration capacity to the municipal treatment plant are obvious.

SECTION X

COST ESTIMATES

In this Section estimates of the capital and operating costs of a biological system designed to remove nearly all of the phenol and ammonia from excess ammonia liquor are developed. Other contaminates such as C.O.D., cyanide and thiocyanate will have smaller percentage removals. The costs developed here are not intended as firm estimates for an actual treatment system. Rather, they are the most probable costs based on available but incomplete technology. The basis for the estimates is a scale-up of the pilot system used in this study. As described in previous sections, numerous problems were encountered during the operation of this system. Many of these problems were solved during the course of the study but others went unresolved. Additional development work will be required to define the unanswered questions before the system can be considered for full scale application. This development work may have a substantial impact on the actual costs. For this reason, the following estimates should be used only for evaluating the need and potential return of further development work.

A coke plant producing 33,000 tons per month (TPM) was selected as the basis for the cost evaluation. This size system is representative of a large number of existing coke plants in this country. With only minor adjustments, the costs developed here should be applicable to many existing facilities. In those cases where scale-up or scale-down is necessary, it is recommended that the logarithmic method frequently used in chemical engineering be employed to adjust the capital cost. This method is expressed as follows:

$$Cn = r^{x} Ce$$

where Cn is the new plant cost, Ce is the estimated cost from this report, r is the ratio of new waste volume to 40,000 gpd, and x is the scaling factor. A value for x of 0.65 is suggested.

The production of 33,000 TPM coke from coal with 5 percent moisture will result in the discharge of approximately 40,000 gallons per day (gpd) of excess ammonia liquor. Typically this waste will contain 6000 ppm (2000 lbs/day) C.O.D. and 4000 ppm (1350 lbs/day) NH_3-N. It is assumed that this waste will be diluted to 50 percent strength (80,000 gpd) before treatment in the carbonaceous removal unit. The carbonaceous removal unit effluent will then be diluted to 25 percent strength (320,000 gpd) prior to treatment in the nitrification and denitrification units. At these dilutions 80 percent C.O.D. removal and 95 percent removal of NH_3-N is expected. The capital cost of the three stage treatment system designed to handle this waste volume is estimated at $995,000. This cost is for a battery limits plant located on a developed site. A breakdown of the estimate is given in Table 20.

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TABLE 20: CAPITAL COST E.A.L. BIOLOGICAL TREATMENT

	DESIGN CRITERIA	UNIT SIZE	COST
I. CARBONACEOUS REMOVAL UNIT			
E.A.L. Storage Tank	48 hr. det.	80,000 gal	$ 21,000
Aeration Tank	24 hr. det.	80,000	27,000
Clarifier	350 gpd/ft^2	20 ft dia.	30,000
Surface Aerator	2.5 lbs. O_2/hp hr	40 hp	11,000
Transfer Pumps (2)		30 gpm	2,000
Sludge Recycle Pumps (2)		60 gpm	4,000
Phosphoric Acid Feed	1 l/m gal E.A.L.	10 gpd	10,000
Antifoam Feed	67 ml/m gal E.A.L.	1 gpd	10,000
Sludge Drying Bed			15,000
Structural Steel			12,000
Piping and Valves			35,000
Electrical and Instrumentation			50,000
	Sub Total		$227,000
II. NITRIFICATION UNIT			
Aeration Tank	24 hr. det.	320,000 gal	$ 73,000
Clarifier	350 gpd/ft^2	35 ft dia.	53,000
Surface Aerators (2)	2.5 lb. O_2/hp hr.	45 hp	24,000
Sludge Recycle Pumps (2)	200 gpm		6,000
Sodium Carbonate & Lime Addition			30,000
Structural Steel			15,000
Piping and Valves			40,000
Electrical and Instrumentation			50,000
	Sub Total		$296,000
III. DENITRIFICATION UNIT			
Mix Tank	8 hr. det.	110,000 gal	$ 36,000
Air Flotation Tank	700 gpd/ft^2	25 ft. dia	53,000
Mixers (2)	0.1 hp/m gal.	6 hp	10,000
Sludge Recycle Pumps		200 gpm	6,000
Molasses Addition			15,000
Structural Steel			15,000
Piping and Valves			40,000
Electrical and Instrumentation			50,000
	Sub Total		$225,000
	TOTAL DIRECT COSTS		$748,000
	INDIRECT COSTS		$247,000
	TOTAL PROJECT COST		$995,000

The costs presented in Table 20 are based on scale-up of the pilot plant described in Section VI. To solve some of the operating problems encountered during the pilot study, four modifications to the original design were made. Excess ammonia liquor storage was increased from 24 hours to 48 hours to provide more cooling and equalization. The system was designed for gravity flow between treatment modules to eliminate the transfer stations. Caustic addition to the nitrification unit was replaced with separate systems for the continuous addition of lime and soda ash. And, the denitrification unit final clarifier was converted to an air flotation system to eliminate biological solids losses from sludge bulking.

The operating cost of the system is estimated at $230,500 per year. This estimate reflects current steel industry costs for materials, utilities, and labor. A breakdown is given in Table 21. For a 33,000 TPM plant, the unit treatment cost is $15.78/1000 gallons. In terms of production, this is an increase of $0.58/net ton coke. If it is assumed that production cost above initial coal cost is $7.00 per net ton, biological waste treatment would represent a cost increase of about 8.7 percent.

In evaluating the operating costs, two items warrant further discussion. First, it was assumed that hydrated lime and sodium carbonate would be used in the nitrification unit for pH control and a source of inorganic carbon. There are a number of compounds or combinations of compounds that could be used to supply these requirements. A cost comparison of four possible chemical systems is given in Table 22. As shown, the limestone system is the most economical from a chemical cost standpoint. The requirements for handling larger tonnages of limestone and increased amounts of waste sludge resulting from unreacted limestone outweigh the cost advantage, however. For this reason, the sodium carbonate-hydrated lime system was selected as the most practical method of pH control and source of inorganic carbon.

The second item is the use of molasses as a source of organic carbon in the denitrification unit. This carbon requirement could be supplied with a variety of materials. Almost any organic compound which is water soluble and biodegradable could be used. The economics of several materials were evaluated during the study. A summary of the evaluation is given in Table 23. Molasses is the least expensive of the materials considered. For this reason, it was used for the cost evaluation. In some parts of the country, however, molasses may not be available. In these areas organic carbon costs should be developed around methanol. This is the most economical alternate and a material that has been reported successful in denitrification by numerous investigators.

TABLE 21: OPERATING COST BIOLOGICAL TREATMENT

Operation: 3 turns/day, 365 days/year
Waste Volume: 40,000 gpd E.A.L.
Fixed Investment: $995,000

DIRECT COSTS	UNITS/YR.	$/UNIT	$/YR.
Materials:			
Molasses	700 Tons	24	17,000
Sodium Carbonate	600 Tons	50	30,000
Hydrated Lime	720 Tons	20	14,400
Phosphoric Acid (75%)	20 Tons	226	4,500
Tributyl Phosphate (100%)	1.18 Tons	1170	1,380
Utilities:			
Steam	55,000 mm lbs.	$ 0.75	41,000
Water	100 mm gals.	20.00	2,000
Electricity	1.10 mm kwh	0.01	11,000
INDIRECT COSTS			
Operating Labor	4 man	15,000	60,000
Maintenance Labor and Material	5% fixed cost		49,220
	Total Operating Cost		$230,500
	(Excluding Interest and Depreciation)		

Unit Operating Costs: $15.78/1000 gals. E.A.L.

$0.58/Ton Coke

TABLE 22: COST COMPARISONS OF NITRIFICATION CHEMICAL REQUIREMENTS

Waste Volume: 40,000 gpd E.A.L.
Ammonia - Nitrogen: 4000 ppm (1350#/day)

CHEMICALS	UNITS/YR.	$/UNIT	$/YR.
Limestone Only*			
Crushed Limestone	3070 Tons	12	$ 36,800
Soda Ash Only			
Granular Sodium Carbonate	1630 Tons	50	$ 81,000
Soda Ash and Caustic			
Granular Sodium Carbonate	600 Tons	50	30,000
Liquid (50%) Sodium Hydroxide	1550 Tons	50	77,500
TOTAL			$225,300
Soda Ash and Hydrated Lime			
Granular Sodium Carbonate	600 Tons	50	30,000
Powdered Calcium Hydroxide	720 Tons	20	14,400
TOTAL			$ 44,400

TABLE 23: COST COMPARISON OF ORGANICS FOR DENITRIFICATION

Waste Volume:	40,000 gpd E.A.L.
Ammonia - Nitrogen:	4000 ppm (1350#/day)

	THEORETICAL REQUIREMENTS* #/# NH_3-N	UNITS/YR.	$/UNIT	$/YR.
Sucrose	2.59	640 Tons	220	141,000
Formaldehyde	2.59	640 Tons	216	136,000
Methylethylketone (MEK)	1.24	305 Tons	210	64,000
Acetone	1.30	320 Tons	118	38,000
Methanol	1.90	468 Tons	82	38,000
Molasses	2.85	700 Tons	24	17,000

*Assuming 50% as nitrate and 50% as nitrite.

It is apparent from the estimates developed above that the biggest percentage of the cost for biological treatment is ammonia removal. Seventy percent of the capital cost and 80 percent of the operating cost can be directly attributed to nitrification and denitrification. The phenol removal system represents only 30 percent of the capital and 20 percent of the operating costs.

SECTION XI

ACKNOWLEDGEMENTS

The laboratory and field studies reported herein were carried out by representatives of Armco Environmental Engineering and the Water Resources Fellowship at Carnegie - Mellon University.

The staff of the Water Resources Fellowship sponsored by the American Iron and Steel Institute are recognized for their very important role in performing laboratory studies and evaluating pilot plant data. Special recognition is given to Dr. William R. Samples formerly Senior Fellow and Head of the Water Resources Fellowship, for his generous assistance without which this project could not have been completed.

Mr. J. E. Barker and Mr. R. J. Thompson of Armco Environmental Engineering are recognized for their contributions in directing and coordinating the research and development effort on the project.

Mr. William Chadick and other representatives of the Houston Works of Armco Steel Corporation are recognized for their contributions and cooperation during the course of the study.

The partial financial support of the study by the American Iron and Steel Institute and the Environmental Protection Agency is hereby acknowledged.

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SECTION XIII

PUBLICATIONS

The work performed during the pilot study has been previously described in the following publication.

Barker, John E. and Thompson, Ronald J.,
"BIOLOGICAL OXIDATION OF COKE PLANT WASTE"
Presented at Chicago Regional Technical
Meeting of A.I.S.I., October 14, 1971

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SECTION XIV

GLOSSARY

Aerobe - organisms which require molecular oxygen.
Anaerobe - organisms which live only in the absence of molecular oxygen.
Autotroph - organisms that rely entirely on inorganic compounds for nutritional requirements.

BOD-5 - 5-day, 20°C biochemical oxygen demand.

C - substrate concentration in reactor.
C_{COD} - COD concentration (mg/l).
C_D - dilution water conductivity.
C_e - estimated plant cost.
C_E - effluent conductivity or substrate concentration.
C_I - influent substrate concentration.
C_L - liquor conductivity.
C_n - new plant cost.
C_{NO_2} - nitrate concentration (mg/l).
C_{NO_3} - nitrate concentration (mg/l).
cm^3/min. - cubic centimeters per minute.
COD - chemical oxygen demand.
Chemosynthetic - organisms which depend on oxidation-reduction reactions of inorganic substrates for energy for growth.
Complete-mix - a system in which the influent is mixed immediately with the entire contents of the vessel resulting in a mixture whose properties are uniform and identical with those of the effluent.

dia. - diameter.
D_{COD} - Stoichiometric COD dosage (mg/l).

e^- - electron
election acceptor - that material that is reduced in biological reactions. In aerobic systems it is oxygen; in the anaerobic denitrification system it is nitrogen.
epl - equivalents per liter.

facultative - organisms which can live in either the presence or absence of molecular oxygen.
ft. - foot.
F - free energy

gal. - gallons.
gpd - gallons per day.
gal/day/ft^2 - gallons per day per square foot.

heterotroph - organisms which utilize organic carbon for energy and growth.
hp - horsepower.
hydrogen acceptor - the oxidizing agent in biological reactions.
hydrogen donor - the oxidized substrate in biological reactions.

kcal - kilocalories.
kg/cal/mole - kilogram-calories per mole.
K - proportionality constant.
Km - modified constant.

lime-distilled - excess ammonia liquor which has been stripped of fixed ammonia by increasing the pH to about 11.0 with lime and passing it through a still.

meq/l - milliequivalents per liter.
mgd - million gallons per day.
mg/l - milligrams per liter.
ml/min. - milliliters per minute.

OC - organic carbon.

ppb - parts per billion.
ppm - parts per million.

Q - volumetric flow in the system.
Q_D - quantity of dilution water.
Q_L - quantity of liquor.

r - ratio of new to assumed waste volume.
redox - oxidation-reduction potential.

S - viable organism concentration in reactor.
Seechi disk - a target plate mounted on a calibrated rod which is used to determine the relative turbidity of water.
sludge bulking - the condition where the solid mass floats in the final clarifier of a biological treatment plant. This condition is frequently caused by the denitrification and the formation of nitrogen gas in the sludge solids.
spent pickle liquor - waste acid which is nearly saturated with iron from acid cleaning or pickling steel.
SWD - side wall depth.

T - residence time in reactor
T_{COD} - total required COD (mg/l).
TPM - tons per month.

UMHOS/CM^2 - micro-ohms per square centimeter.

V - volume of reactor.

X - scaling factor.

SECTION XV

APPENDIXES

A-1 Analytical Data for Excess Ammoniacal Liquor

A-2 Analytical Data for Effluent from the Carbonacious Unit

A-3 Analytical Data for Effluent from the Nitrification Unit

A-4 Analytical Data for Effluent from the Denitrification Unit

B-1 Analytical and Operational Data for the Carbonaceous Unit

B-2 Analytical and Operational Data for the Nitrification Unit

B-3 Analytical and Operational Data for the Denitrification Unit

C Alkalinity Balance for Nitrification

APPENDIX A-1. BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES
ANALYTICAL DATA FOR EXCESS AMMONIACAL LIQUOR

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRITE	NITRATE			
2-1-70		8.6	1580														
2	64	8.6	1460	689			505	12	250		1880	101					13800
3	53	8.6	1340														
4	52	8.5	1280	706				8			1848						17000
5	67	8.2	1000														
6	65	8.8	2060	587				30			1967						14200
7	62	8.8	1740														
8	67	8.6	1660														
9	62	8.8	1680	773			410	21	210	7	1910	115					14100
10	55	8.9	1660														
11	63	8.6	1530	809				17			1862						14100
12	65	8.6	1410														
13	67	8.7	1290	620				13			1820						13800
14	72	9.0	2920														
15	73	9.0	2700														
16	60	9.0	2590	641			501	33	190	50	1820	88					10700
17	59	9.0	2510														
18	68	8.9	2720	880				32			1780						11100
19	72	8.9	2370														
20	61	8.7	2300	677				37			1988						12500
21	68	8.7	2240														
22	61	8.7	1940														
23	66	8.9	1970	567			525	47	240	23	2114	92					11600
24	65	8.8	1960														
25	65	8.8	1830	890				24			1900						12700
26	60	8.7	1810														
27	62	8.6	1540	705				21			1860						13300
28	64	8.6	1620														
3-1-70	69	8.6	1400														
2	69	8.8	2280	702			528	24	256	20	1950	81					12700
3																	
4	74	8.8	2030	913				19			1890						12700
5	66	8.9	2060														
6	66	8.9	2030	703				15			1830						11700
7	61	8.9	1870														
8	64	8.7	1710														
9	64	8.6	1675	1210			778	20	250	4	1980	104					13800
10	70	8.7	1645														
11	66	8.6	1485	760				7.3			1720					3130	12400
12	57	8.7	1580														
13	58	8.8	1552	1533				14			1940					3644	14000
14	60	8.6	1475														
15	61	8.7	1455														
16	70	8.5	1375	1550	3630	2330	765	12	240		1920	88				3704	13800
17	65	8.5	1200														
18	63	8.4	1300	1167				20			1880						13200
19	77	8.4	1150														
20		8.3	1100	1360				8.1			1860						14700
21	60	8.8	1795														
22	60	8.7	1750														
23	62	8.6	1580	1300			645	13	286		1760	97					12400
24	67	8.9	1625														
25	69	8.8	1640	1140				37			2250						13300
26	65	8.9	1625														
27	64	8.3	1200	1980				8.6			1715						12400
28	72	8.9	2700														
29	63	9.2	2700														
30	63	9.0	2750	2220			930	34	175	23	2080	81					12700
31	69	8.8	2600														
4-1-70	69	8.8	2550	1708				16			2010						14210
2	59	8.7	2390														
3	68	8.9	2400	3208				44			2000						12200
4	66	8.8	2075														
5	69	8.8	2250														
6	66	8.8	2020	2460	4010	2340	928	19	274	7	1920	69			144		12400
7	68	8.7	2085														
8	75	8.7	1950	2410				11			1890						12500
9	73	8.8	2070														
10	71	8.9	1985	3610				33			3000						20400

APPENDIX A-1: page 2 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
4-11-70																	
12																	
13	72	8.6	1700	2880			730	13	240	2	1760						12000
14		8.4	1500														
15	75	8.5	2000	3947				35			3810						24300
16		8.6	1700														
17	69	8.5	1490	2327				18			3230						21600
18	75	8.4	1500														
19	74	8.5	1640														
20		8.3	2700	3440			1130	17	394	2	3330	253					24600
21	72	8.5	1320														
22	79	8.3	1220	2842				26			4240						27000
23	75	8.6	1850														
24	67	8.4	1340	2470				17			4100						25800
25	76	8.4	1490														
26	94	8.6	1900														
27	68	8.5	1440	1990			846	21	548	0	3500	199					23400
28	74	8.2	1070														
29		8.2	1020	1918				24			3740						23900
30	78	8.5	1520														
5-1-70	66	8.4	1200	1550				34			3190						20580
2	68	8.4	1300														
3	74	8.4	1425														
4	66	8.5	1400	966	3400	1710	556	23	400	2	3210	118				44	21800
5		8.5	1500														
6	83	8.4	1360	1619				30			3490						20900
7	77	8.7	2200														
8		8.5	2000	1720				31			3330						19400
9	77	8.8	1750														
10	80	8.5	1425														
11	76	8.5	1250	1580			665	33	366	3	3370	196					21400
12	81	8.6	890														
13	74	8.6	1860	1500				35			3640						24300
14	79	8.7	1800														
15	78	8.5	1650	1515				34			3610						22400
16	69	8.5	1380														
17	70	8.6	1750														
18	75	8.6	1750	2380			850	11	230	2	3250	193					19500
19	78	8.5	1590														
20		8.6	1960	822				37		4	3540						21900
21	90	8.5	1740														
22		8.6	1900	791				37			3420						20800
23	84	8.2	1400														
24	78	8.5	1500														
25	80	8.4	1250	1060			634	35	98	6	3150	224					21200
26	88	8.8	2350														
27	88	8.7	2040	1209				35			3080						18000
28	71	8.6	2040														
29	80	8.7	2000	928				24			3120						19700
30	81	8.6	1740														
31	78	8.5	1500														
6-1-70				1370	4140	2370	760	34	356	4	3150	230			70		26000
2	88	8.7	2200														
3	79	8.6	2000	1200				42			3300						20000
4	88	8.6	1900														
5	78	8.6	1900	2980				41			3570						20800
6	101	8.7	2200														
7	84	8.7	2125														
8	87	8.7	1880	1020			700	24	410	0	3420	14					21300
9	82	8.6	1690														
10	85	8.6	1810	713				27			3860						23800
11	83	8.5	1720														
12	85	8.5	1530	1414				40			3770						22400
13	85	8.5	1480														
14	87	8.6	1550														
15	83	6.6	1400	1400			906	20	360	0	3930	375					25500
16	77	8.7	1670														
17		8.5	1240	675	3620			27			3720						29600
18	87	8.6	1450														

APPENDIX A-1: page 3 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
6-19-70	92	8.5	1300	272	1770			19			3820						29000
20	86	8.7	1790														
21	84	8.6	1400														
22	83	8.5	1400	578	3380		650	24	290		4100	179					29600
23		8.6	1500														
24	90	8.7	1680	586	3650			31			4470						32100
25	87	8.6	1800														
26	94	8.6	1680	272	3340			28			3710						24800
27	91	8.7	1950														
28	88	8.5	1680														
29	89	8.3	1300	521	3390		650	17	370		3650	179					18000
30	89	8.4	1300														
7-1-70	89	8.4	1330	602	3440			30			3710						25600
2	93	8.3	1180														
3	88	8.5	1380	834	3190			25			3720						26500
4	96	8.4	1250														
5	85	8.5	1425														
6	85	8.3	1380		3440	1830	580	29	350		3440	182			61		25200
7	89	8.2	1200														
8	87	8.2	1100		3370			19			3500						23900
9	94	8.4	1700														
10	93	8.5	1440		2990			34			3560						26000
11	87	8.4	1200														
12	88	8.4	1500														
13	84	8.4	1280		3160		485	28	304		3790	154					28700
14	87	8.4	1450														
15	88	8.4	1490		2920			31			3670						28100
16	88	8.3	1200														
17	88	8.4	1150		2880			[illegible]			3630						27300
18	88	8.4	1350														
19	88	8.3	1100														
20	86	8.3	1200		2910		540	24	314		3280	258					24000
21	88	8.3	1150														
22	85	8.4	1135		2700			24			3280						23100
23	81	8.6	1450														
24	91	8.3	960		2960			27			3260						26300
25	98	8.6	1550														
26	88	8.5	1515														
27	88	8.4	1640														
28		8.4	1550														
29	90	8.3	1220	950	3140			24			3400						23500
30																	
31	92	8.4	1600		1310			27			3200						23800
8-1-80	87	8.4	1400														
2	89	8.5	1510														
3	85	8.4	1350	1620	2920		420	27	300	2	2720	104			50		20700
4	93	8.6	1600														
5	90	8.5	1400		2580			21			2770						20000
6	88	8.6	1750														
7	88	8.4	1290		2729			23			2650						18900
8	91	8.6	1420														
9	102	8.5	1650														
10	90	8.5	1370		2790		500	25	324		2730	106					20000
11	95	8.4	1130														
12	98	8.5	1720		2740			21			2700						19800
13	88	8.5	1400														
14	86	8.5	1550		2970			33			3230						22300
15	99	8.6	1650														
16	88	8.6	1480														
17	108	8.7	1580		3079		550	26	290	4	2580	120					17800
18	90	8.6	1150														
19	106	8.6	1580		2910			26			2690						18000
20	91	8.7	2150														
21	92	8.6	1600	880	2860			17			2530						18400
22	86	8.6	1390														
23	96	8.7	1610														
24	108	8.6	1560		4010		706	19	426	2	3900	143					27500
25	90	8.5	1925														
26	83	8.9	1880		2360			28			1690						10000

APPENDIX A-1: page 4 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
8-27-70	78	8.2	1540														
28	85	8.8	2100		2010			24			1690						12100
29	83	8.7	1850														
30	84	8.6	1270														
31	88	8.6	1950		5680		1240	14.1	440	2	3230	137					22800
9-1-70	79	8.5	1250														
2	83	8.6	2045		7700			17			3040						22000
3	84	8.6	1230														
4	87	8.6	2080		7390			12			2930						20700
5	85	8.6	2100														
6	89	8.9	1720														
7	86	8.6	1700														
8	87	8.5	1950		7910		1700	8.7	530	1	3120	146					21800
9	90	8.5	1920		9664			13			3920						26900
10	85	8.5	2150														
11	84	8.6	2160		9530		1980	15			4200						28600
12	84	8.7	2580														
13	84	8.6	2640														
14	91	8.5	1900		8500	6170	1740	15	768	1	4410	230			49		30100
15	87	8.6	2700														
16	81	8.5	1970		9040			12			4200						28700
17	87	8.6	2340														
18	85	8.6	2300		8610			20			4000						28600
19	84	8.6	2250														
20	87	8.6	2300														
21	84	8.5	2020		9390		1900	24	1540	1	4160	196					28200
22	90	8.6	2400														
23					8200			15			3370						23000
24	81	8.8	2340														
25	84	8.5	2350		9490			26			3320						20800
26	80	8.4	2230														
27	75	8.6	2280														
28	72	8.7	2280		9680		2150	13	628	2	3370	165					23200
29	70	8.7	2260														
30	79	8.5	2250		9550			20			3780						23800
10-1-70	75	8.6	1920														
2	85	8.7	3050		10900			21			4170						26800
3	81	8.7	3025														
4	79	8.6	2650														
5	82	8.6	2760		10600	5790	2380	25	1100	2	4120	188			0. 75		28800
6	94	8.6	2600														
7	83	8.4	2640		10100			23			4000						27100
8	87	8.5	2450														
9	64	8.5	2120		9790			14			3950						28100
10	70	8.7	2500														
11	71	8.7	2480														
12	72	8.7	2450		8910		652	21	660	4	3930	260					28800
13	70	8.7	2260														
14	68	8.7	2270		10200			11			3750						27100
15	69	8.6	2275														
16	67	8.6	2000		9230			8			3800						27800
17	67	8.6	2000														
18	65	8.7	2010														
19	65	8.8	2300														
20	65	8.9	2500														
21	67	8.8	2600		6960			25			4100						28600
22	73	8.7	2315														
23	76	8.7	1975		8450		8.0				4370						29900
24	70	8.7	2130														
25	72	8.7	2140														
26	76	8.6	1850		9142		1900	12	480		4130	230					29600
27	80	8.6	1800														
28	76	8.7	1800		6170			28			3670						26500
29	64	8.6	1660														
30	66	8.5	1660		5320			20			3780						27200
31	65	8.6	1850														
11-1-70	67	8.6	1820														
2	64	8.6	1660		4773	2460	915	26	540	3	3440	204			34		25100
3	62	8.8	975														

APPEND[illegible]: page 5 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
11-4-70	62	8.8	1880		4920			26			3890						27200
5	59	8.8	2000														
6	66	8.7	2000		15600			52			4400						31700
7	67	8.6	1850														
8	77	8.5	1800														
9	73	8.5	1650		5465		1070	26	640	2	3930	204					28600
10	66	8.5	1680														
11	67	8.4	1470		5210			17			4140						30800
12	68	8.5	1800														
13	67	8.7	2100		5930			12			3700						26600
14	60	8.7	1570														
15	60	8.8	2100														
16	52	8.9	2060		6160		1080	30	540	3	3420	90					24900
17	68	8.8	2130														
18	71	8.7	2180		4620			23			3822						26900
19	68	8.7	2125														
20	72	8.6	1900		5450			18			3470						24800
21	65	8.6	1900														
22	70	8.6	1700														
23	60	8.6	1725		5471		1110	14	560	<1	3530	140					27300
24	49	8.5	1650														
25	86	8.7	2100		5870			30			4120						28700
26	67	8.5	1490														
27	75	8.4	1300		5570			11	11		3540						27100
28	74	8.3	1250														
29	74	8.1	1060														
30	72	8.5	18[illegible]0		5915		1120	20	690	0.4	3900	168					28650
12-1-70	73	8.5	1750														
2	80	8.5	1725		6143			21			3750						27200
3		8.6	1650														
4	73	8.4	1320		6040			13			3720						28200
5	74	8.4	1575														
6	71	8.4	1520														
7	65	8.5	1320		13800	4160	1480	21	692	1	3960	255			60		27500
8	70	8.5	1325														
9	71	8.8	2650		6930			35			4720						33100
10	68	8.9	2550														
11	70	8.8	2300		7220			30			3720						28200
12	57	8.7	2280														
13	58	8.6	2100														
14	57	8.6	2130		5900		1180	31	652	4	4120	176					28300
15	64	8.8	2550														
16	67	8.9	2400		5960			34			4420						31400
17																	
18	70	8.3	1900		5520			24			4260						32200
19	71	8.5	2180														
20	70	8.5	1600														
21	71	8.6	1950		5650		1100	20	640	1	4200	252					31700
22	73	8.6	1800														
23	74	8.4	1600		6560			22			2560						30600
24	66	8.6	1900														
25	66	8.5	1930		6400			25			2510						28200
26	54	8.6	1650														
27	54	8.5	1560														
28	65	8.6	2450		6700		1290	23	648	4	2410	700					28900
29	70	8.6	2180														
30	68	8.7	2560		6450			20			2030						30300
31	60	8.7	2425														
1-1-71	58	8.6	2170		6580			14			1960						28700
2	62	8.7	1920														
3	70	8.7	2270														
4	57	8.7	2020		7210	4030	1310	18	668	1	2060	2300			52		30100
5	50	8.6	1950														
6	50	8.7	1980		6170			12			1974						31100
7	44	8.6	2050														
8	42	8.5	1800		5920			27			2000						32900
9	50	8.8	2500														
10	63	8.8	2425														
11	65	8.7	2220		5390		1010	28	612	2	2130	2100					29600

APPENDIX A-1: page 6 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
1-12-71	80	8.7	2700														
13	82	8.6	2700		5790			21			3950						28800
14	78	8.6	2450														
15	75	8.6	2050		5763			21			3976						29600
16	62	8.7	2450														
17	65	8.7	2460														
18	66	8.7	2210		5940		1200	32	648	2	4450	84					29700

APPENDIX A-2: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES
ANALYTICAL DATA FOR EFFLUENT FROM THE CARBONACEOUS UNIT

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
2-1-70		8.3	374														
2		8.3	393	33			0.1	0.8	32		232	31	0.3				2730
3		8.5	252														
4		8.3	316	44				0.5			230		0.4				2830
5		8.3	362														
6		8.4	269	19				0.5			136		0.4				2000
7		8.4	300														
8		8.4	348														
9		8.3	316	27			0.2	1.0	39		273	34	0.2				2860
10		8.3	363														
11		8.5	323	27				0.7			274		0.3				2930
12		8.4	308														
13		8.2	277	26				0.9			248		0.3				2700
14		8.1	402														
15		8.3	434														
16		8.4	481	33			0.2	0.5	26		225	34	0.4				2230
17		6.5	90														
18		8.4	400	28				0.5			217		0.4				2320
19		8.1	460														
20		8.2	440	29				1.1			267		0.6				2440
21		8.0	460														
22		8.2	420														
23		8.1	350	22			0.7	0.8	38		192	31	0.6				2010
24		7.8	380														
25		8.3	425	20				1.0			251		0.6				2630
26		8.2	400														
27		8.3	370	19				0.9			230		0.6				2510
28		8.3	390														
3-1-70		8.3	375														
2		8.3	330	17			0.1	0.9	32		207	16	0.8				2490
3																	
4		8.4	410	16				1.0			228		1.2				2400
5		8.1	300														
6		8.0	410	14				0.7			190		4.7				2100
7		7.7	350														
8		8.3	280														
9		7.5	110	22			0.1	1.2	22		188	14	34				2430
10		6.8	60														
11		7.5	35	15				1.5			202		41	47		474	2630
12		6.4	50														
13		6.5	70	21				1.0			188		43	38		480	2550
14		6.9	90														
15		6.7	50														
16		6.4	60	22			0.1	3.2	17		225	16	58	39		571	2800
17		6.3	35														
18		6.4	60	11				4.0			168		59				2540
19		6.5	45														
20		6.4	50	20				2.8			230		66				2990
21		8.0	250														
22		8.0	190														
23		6.9	80	23			0.1	1.3	16		266	24	58				3110
24		6.9	125														
25		6.9	70	12			1.6				160		67				2480
26		6.9	85														
27		6.6	50	21			4.3				256		74				3210
28		7.5	125														
29		7.5	180														
30		7.0	90	25			0.0	1.3	12		276	21	63				3410
31		7.2	100														
4-1-70		6.7	150	35				3.2			405		70				4500
2		7.2	170														
3		6.8	75	44				1.6			304						3550
4		7.0	105														
5		8.4	250														
6		8.5	445	323			124	1.9	86		325	22	6.2				3330
7		8.3	520														
8		8.2	470	67				1.3			322		1.0				3280
9		8.5	425														
10		8.5	520	44				0.9			364		0.6				3610

APPENDIX A-2: page 2 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
4-11-70																	
12-																	
13-		8.5	500	74			0.2	1.5	64		399	43	1.0				4000
14		8.5	425														
15		8.2	320	22				0.9			252		0.8				3510
16		8.3	375														
17		8.3	350	44				1.5			599		1.1				5680
18		8.1	380														
19		8.2	360														
20		8.0	310	83			0.1	20	79		788	45	3.7				7480
21		8.1	375														
22		8.0	335	104				6.2			1120		6.3				9820
23		8.1	400														
24		8.1	390	66				4.9			1220		6.3				9860
25		8.2	420														
26		8.2	350														
27		8.2	455	71			0.2	3.7	113		1360	59	2.9				10780
28		8.0	400														
29		8.0	270	92				2.8			1150		6.6				9560
30		8.0	270														
5-1-70		7.7	240	66				2.7			1190		5.4				9390
2		7.8	240														
3		7.0	125														
4		7.8	275	52			1.0	3.3	22	0.2	1170	59	7.3				9730
5		7.9	325														
6		7.8	335	61				3.9			1400		6.9				11000
7		8.2	600														
8		8.2	685	150				5.8			1700		5.1				12500
9		8.5	600														
10		8.3	600														
11		8.2	450	45			0.1	4.3	164		1510	76	5.9				12600
12		8.3	590														
13		8.2	525	60				11			1640		4.6				14000
14		8.3	550														
15		8.2	550	64				4.6			1640		2.3				12200
16		8.3	600														
17		8.2	600														
18		8.2	500	102			0.2	4.7	86		1690	87	1.5				13300
19		8.2	625														
20		8.2	725	247				5.1			2020		1.5				15000
21		8.3	590														
22		8.2	650	62				10			1970		0.7				14700
23		8.2	600														
24		8.2	525														
25		8.0	440	52			0.2	5.4	198		1652	200	1.0				14100
26		8.3	700														
27		8.3	625	1209				35			3080						18000
28		8.4	750														
29		8.3	675	33				5.4			1760		0.5				13200
30		8.3	650														
31		8.2	625														
6-1-70				148			5.0	5.1	180		1720	161	0.5				14900
2		8.3	790														
3		8.0	5[illegible]5	90				10			2100		0.1				14600
4		8.4	990														
5		8.4	920	287				6.2			2440		0.1				16600
6		8.2	860														
7		8.2	950														
8		8.3	975	92			0.57	6.0	620		2560	196	0.3				17400
9		8.3	1360														
10		8.3	1020	59				6.2			2860		0.2				19400
11		8.3	1070														
12		8.3	1010	166				5.5			3040		0.2				20300
13		8.3	990														
14		8.5	980														
15		8.3	450	613			0.60	6.2	340		2940	200	0.5				21700
16		8.4	940														
17		8.1	620	39	1700			9.1			2860		0.3				23500
18		8.3	700														

APPENDIX A-2: page 3 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
6-19-70		8.1	360	24	1030			6			1810						15600
20		8.3	525														
21		8.3	475														
22		8.1	375	51	875		0.34	4.2	240		1820	98	0.2				15100
23		8.2	525														
24		8.2	365	43	955			4.4			2180		0.2				18100
25		8.2	640														
26		8.1	475	22	1000			5			2320		0.4				17800
27		8.2	475														
28		8.1	415														
29		8.0	380	18	667		0.2	4	154		1740	102	0.2				15100
30		8.1	325														
7-1-70		8.0	325	33	719			6.7			1790		0.1				15600
2		8.0	325														
3		8.0	350	53	645			9.1			1840		0.3				15800
4		8.0	425														
5		8.0	430														
6		7.8	280		716		0.2	11	164		1880	42	0.4				15400
7		8.0	500														
8		7.9	520		727			5.6			1920		0.3				15300
9		8.0	375														
10		8.0	350		725			4.7			1760		0.4				14400
11		8.0	355														
12		8.1	400														
13		8.0	325		803		0.2	3.5	174		1580	88	0.3				13800
14		8.0	380														
15		8.0	340		532			3.7			1670		0.2				14900
16		8.0	400														
17		7.8	185		512			3.1			1270		0.4				11200
18		8.0	350														
19		8.0	350														
20		7.9	310		546		0.2	3.5	174		1620	143	0.7				14100
21		8.0	400														
22		8.0	380		793			4.3			1760		0.3				14400
23		8.3	550														
24		8.0	420		867			5.0			2240		0.3				19700
25		8.1	480														
26		8.1	540														
27																	
28		7.9	430														
29		7.7	235	41	1140			5.0			1920		0.3				16400
30		7.9	400														
31		7.9	415		816			6.3			2160		0.4				18000
8-1-70		8.0	525														
2		8.0	550														
3		7.9	415		788		0.3	5.5	190		2220	119	0.4				18800
4		8.2	640														
5		8.0	390		696			5.0			1880		0.3				16500
6		8.2	660														
7		8.0	435		725			4.3			1820		0.6				15100
8		8.2	550														
9		8.1	475		665		0.2	4.7	250		1740	80	1.1				14300
10		8.1	510														
11		8.0	460														
12		8.2	450		695			6.1			1780		1.0				14400
13		8.2	620														
14		8.2	565		707			8.5			1850		0.5				14700
15		8.2	515														
16		8.1	540														
17		8.1	455		777		0.17	4.9	220		1940	92	0.8				15900
18		8.2	530														
19		8.2	475		774			4.5			1700		0.5				13800
20		8.6	720														
21		8.2	470	72	1190			4.6			1670		1.4				14400
22		8.1	525														
23		8.1	445														
24		8.2	535		895		.30	6.0	274	0.6	1710	84	0.5				14700
25		8.2	550														
26		8.0	485		903			5.7			2240		0.3				18400

APPENDIX A-2: page 4 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
8-27-70		7.7	500														
28		8.0	575		900			4.6			1870		0.6				15200
29		8.2	650														
30		8.0	335														
31		8.1	415		693		.22	2.7	144		1040	98	0.8				9630
9-1-70		8.1	500														
2		8.1	575		785			3.3			1530		0.4				14000
3		8.0	575														
4		7.9	490		2960			4.1			1920		0.1				15800
5		8.0	550														
6		7.9	475														
7		7.8	300														
8		7.8	410		1250		0.2	4.3	270		1730	115	0.3				14600
9		7.8	340		1319			5.0			1890		0.2				16300
10		7.8	550														
11		7.8	475		1850		0.90	4.6			2480		0.1				20600
12		8.0	660														
13		7.9	560														
14		7.8	465		2060		1.1	4.6	394		2600	176	0.3				21400
15		8.0	675														
16		7.8	590		2440			2.4			2860		0.6				23200
17		7.9	670														
18		7.7	540		2390			5.4			2630		0.1				22400
19		7.9	625														
20		7.9	575														
21		7.8	475		2380		1.2	5.8	1220		2520	153	<0.1				21500
22		7.9	650														
23					2240			8.4			2480		0.3				20000
24		8.0	640														
25		7.9	550		2020			5.9			2160		0.2				17600
26		7.9	575														
27		7.9	625														
28		7.8	575		1993		11	5.9	394		238	77	0.3				17000
29		8.2	825														
30		7.8	475														
10-1-70		7.9	645														
2		8.1	980														
3		8.0	955														
4		8.0	900														
5		7.9	725		2740		16	5.6	628		2340	80	0.5				19800
6		8.1	725														
7		7.8	560		2330			5.0			2020		0.3				16800
8		7.9	550														
9		7.8	380		1550			3.4			1350		0.4				12500
10		8.0	475														
11		8.1	450														
12		8.0	420		766		0.2	1.7	150		686	99	0.2				6240
13		8.1	420														
14		8.1	380		629			2.0			520		0.3				5100
15		8.0	350														
16		8.0	325		583			1.2			504		0.3				5040
17		8.1	375														
18		8.0	400														
19		8.1	295														
20		8.2	340														
21		8.1	375		602			1.6			658		0.4				6010
22		8.1	350														
23		7.9	330		567			1.8			700		0.5				6600
24		8.0	365														
25		8.0	375														
26		8.0	360		732		0.2	2.9	220		931	74	0.3				8700
27		8.0	345														
28		8.0	400		807			2.8			1140		0.2				11500
29		8.0	425														
30		8.0	480		895			8.5			1510		0.4				12900
31		8.0	525														
11-1-70		8.2	540														
2		8.2	370		592		0.2	3.0	190		1080	62	0.1				9740
3		8.3	525														

APPENDIX A-2: page 5 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
11-4-70		8.3	560		672			3.1			1200		0.3				11100
5		8.4	570														
6		8.2	725		1680			6.4			1760		0.4				15100
7		8.2	690														
8		8.1	650														
9		8.0	575		928		0.6	5.0	290		1880	95	0.2				15900
10		8.0	595														
11		8.0	580		1030			5.5			2070		0.3				17600
12		8.1	625														
13		8.2	625		1080			12			1920		0.6				15900
14		8.3	660														
15		8.3	750														
16		8.4	825		1280		4.3	12	306		1670	70	0.4				14800
17		8.2	1625														
18		8.2	575		697			3.8			1155		0.2				9810
19		8.2	520														
20		8.2	425		658			2.4			763		0.5				6940
21		8.2	400														
22		8.2	400														
23		8.2	400		582		0.4	2.7	140	<1	791	84	0.2				7550
24		8.2	380														
25		8.2	390		419			2.6			686		0.2				6330
26		8.2	380														
27		8.0	325		344			2.2			609		0.2				6040
28		8.0	300														
29		8.0	280														
30		8.1	320		445		0.1	2.9	180		777	63	0.3				7160
12-1-70		8.1	350														
2		8.1	340		417			4.9			728		0.8				6930
3		8.2	350														
4		8.0	320		516			4.0			1280		0.2				11200
5		8.1	400														
6		8.1	350														
7		8.0	280		538		0.1	3.3	250		1250	48	0.4				11300
8		8.0	300														
9		8.2	490		517			4.8			1200		0.6				10600
10		8.4	600														
11		8.3	650		782			7.4			1730		0.3				14800
12		8.2	570														
13		8.1	525														
14		8.1	510		840		0.2	5.0	280		1860	37	0.5				16000
15		8.3	600														
16		8.3	525		729			6.4			1760		0.3				14500
17																	
18		8.3	500		688			6.3			1590		0.1				13400
19		8.1	500														
20		8.2	520														
21		8.1	440		698		0.1	6.1	280		1920	41	0.3				16000
22		8.1	510														
23		8.0	450		692			6.3			1130		0.3				16500
[illegible]		8.0	410														
25		8.0	460		660			4.7			1090		0.3				16000
26		8.1	460														
27		8.1	580														
28		8.1	625		757		0.3	5.6	284		1140	393	0.3				15700
29		8.2	650														
30		8.2	660		654			5.0			861		0.5				15600
31		8.2	625														
1-1-70		8.5	510														
2		8.3	645		594			4.3			805		0.5				14200
3		8.2	600														
4		8.3	580		646		0.2	4.4	284		784	931	0.8				14200
5		8.3	550														
6		8.2	450		727			5.0			826		0.5				15300
7		8.2	325														
8		8.0	350		767			4.8			693		0.3				13600
9		8.2	575														
10		8.2	415														
11		8.1	424		764		0.3	5.4	294		784	910	0.2				14400

APPENDIX A-2: page 6 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
1-12-70		8.2	450														
13		8.1	525		754			5.7			1690		0.6				14200
14		8.2	615														
15		8.1	540		659			5.4			1680		0.8				14000
16		8.2	625														
17		8.3	575														
18		8.2	525		689		0.2	4.7	284		1670	70	0.8				13500
19																	
20					674			3.8			1250		1.2				11700

APPENDIX A-3: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES

ANALYTICAL DATA FOR EFFLUENT FROM THE NITRIFICATION UNIT

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
2-1-70		6.5	136														
2		6.6	85	54							213		47	48			2920
3		6.7	86														
4		7.5	95	35							186		33	34			2790
5		6.4	174														
6		6.4	47	37							160		47	39			2620
7		6.4	48														
8		6.9	91														
9		6.7	79	39							200		56	48			2860
10		7.0	71														
11		6.9	95	36							237		52	48			3100
12		7.0	95														
13		6.6	869	36							225		51	50			2990
14		7.2	118														
15		7.2	162														
16		6.5	126	39							161		71	55			2390
17		8.5	443														
18		6.8	105	36							160		70	59			2420
19		6.3	80														
20		6.4	70	27							200		74	59			2500
21		6.4	100														
22		6.6	100														
23		6.5	90	27							164		68	51			2280
24		6.3	90														
25		6.3	90	21							141		70	63			2570
26		6.3	110														
27		6.2	75	23							178		70	64			2810
28		6.2	45														
3-1-70		6.4	45														
2		6.4	50	21							167		70	56			2890
3																	
4		6.3	45	17							132		80	67			2580
5		6.4	65														
6		6.2	60	16							81		97	75			2100
7		6.7	75														
8		6.7	50														
9		6.7	50	19							97		90	91			2630
10		6.2	60														
11		6.4	40	18					10		136		93	94		486	2840
12		6.0	55														
13		6.4	40	10					9		151		84	76		486	2820
14		6.5	100														
15		6.5	50														
16		6.3	45	16					10		178		87	69		523	2840
17		6.1	35														
18		6.0	60	13							206		87	64			3250
19		6.3	55														
20		6.3	45	16							147		95	73			2790
21		6.5	120														
22		6.5	55														
23		7.0	75	18							241		102	63			3030
24		6.5	105														
25		6.7	70	13							221		96	75			3110
26		6.5	75														
27		6.3	50	23							197		126	90			3250
28		6.4	45														
29		6.3	125														
30		6.2	55	16							216		87	110			3520
31		6.2	55														
4-1-70		6.0	70	23							310		96	107			
2		6.4	68														
3		6.5	90	39							302		131	147			4230
4		6.5	60														
5		7.1	75														
6		8.3	225	27							144		122	128			3860
7		6.6	40														
8		6.3	30	16							62		96	95			2500
9		6.3	30														
10		6.4	55	15							29		135	116			2520

APPENDIX A-3: page 2 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
4-11-70																	
12																	
13		6.8	500	55													
14		6.4	40								136		160	182			4230
15		6.2	35	28													
16		6.7	50								223		83	122			4040
17		6.5	45	16													
18		6.4	50								193		103	230			5400
19		6.7	45														
20		6.5	40	48													
21		6.9	60								416		192	254			7750
22		6.8	60	74													
23		6.7	75								728		224	220			10300
24		6.7	65	86													
25		6.7	70								994		130	172			10300
26		6.9	75														
27		6.6	65	74													
28		8.0	380								609		115	185			10780
29		7.9	185	88													
30		7.5	135								840		296	283			11300
5-1-70		6.8	70	49													
2		6.8	75								644		400	405			11300
3		7.7	240	27													
4		6.8	80								553		441	369			12800
5		6.8	105														
6		9.0	1120	41													
7		8.6	715								777		366	314			11400
8		8.3	500	142													
9		8.4	450								1360		61	70			12200
10		8.0	300														
11		7.6	120	30													
12		6.4	15								567		34	34			5940
13		6.2	35	9													
14		8.2	300								259		66	52			3530
15		8.3	400	48													
16		7.8	215								1140		45	53			11000
17		7.5	160														
18		7.5	180	109													
19		7.5	145								1620		21	47			13000
20		6.6	40	48													
21		6.3	40								875		50	63			8400
22		6.7	25	4													
23		6.4	20								364		63	66			4310
24		6.4	20														
25		6.7	25	4													
26		7.2	135								182		54	106			3370
27		7.5	100	24													
28		7.5	140								749		131	135			8150
29		7.8	220	26													
30		8.0	370								1430		103	96			12900
31		8.0	360														
6-1-70				29													
2		7.9	175								1740		4.3	7.4			15600
3		7.9	140	22													
4		8.2	250								567		0.6	1.2			4640
5		8.0	245	27													
6		8.0	240								343		0.5	0.51			3310
7		8.0	240														
8		7.0	205	39													
9		8.0	180								154		4.8	3.4			1800
10		8.0	145	44													
11		7.3	75								112		10	4.8			1940
12		6.7	20	73													
13		6.3	25								106		17	3.9			1910
14		6.6	20														
15		7.0	75	73													
16		6.1	20								8		66	91			2060
17		6.7	25	39													
18		6.4	25								36		108	105			2540

APPENDIX A-3: page 3 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
6-19-70		8.0	105	24							136		111	140			4020
20		6.7	40														
21		6.8	35														
22		6.5	25	17	219						100		183	154			3890
23		6.4	25														
24		6.8	70	43							134		142	174			4470
25		6.8	50														
26		6.4	40	6	213						61		174	186			3840
27		6.4	40														
28		6.6	60														
29		7.0	75	7	277						69		200	199			4690
30		8.1	125														
7-1-70		7.6	190	18	404						27		223	298			5680
2		9.9	400														
3		8.3	210	21	227						197		173	203			4480
4		7.5	100														
5		6.4	25														
6		6.5	25		89						228		60	63			
7		6.5	25														
8		6.6	35		318						262		161	142			5180
9		6.9	50														
10		6.9	50		343						232		109	149			4820
11		6.8	40														
12		6.8	35														
13		6.8	35		309						214		102	135			4730
14		6.7	30														
15		6.7	50		373						239		124	162			5550
16		6.7	50														
17		6.8	40		380						277		124	158			5610
18		7.7	130														
19		6.7	30														
20		6.7	30		295						361		147	115			5620
21		6.6	65														
22		6.7	55		381						339		142	131			5830
23		7.2	80														
24		8.0	220		426						899		77	88			10200
25		8.0	275														
26		7.8	245														
27																	
28		7.7	230														
29		7.7	135	32	555						1090		32	4.2			1020
30		8.0	200														
31		7.9	145		140						378		4.9	3.2			4040
8-1-70		8.0	160														
2		7.8	120														
3		7.4	85		58						123		43	25			2170
4		6.7	35														
5		6.6	25	31	81						104		29	47			2080
6		6.4	25														
7		6.8	25		94						104		38	51			2030
8		6.7	60														
9		6.6	20														
10		6.6	20		85						137		35	47			2260
11		6.5	60														
12		6.5	60		74						126		38	47			2240
13		6.2	50														
14		6.6	55		82						48		25	41			1430
15		6.6	45														
16		6.6	20														
17		6.5	2.0		66						73		41	41			1690
18		6.6	15														
19		6.4	55		90						82		45	43			1740
20		6.4	20														
21		8.8	345	25	171						161		40	32			2640
22		8.5	255														
23		8.4	210														
24		8.4	205		142						207		4.8	6.9			2680
25		8.3	220														
26		8.1	185		178						326		11	15			3850

APPENDIX A-3: page 4 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
8-27-70		7.7	165														
28		7.8	140		218						482		13	21			4990
29		7.5	100														
30		6.7	35														
31		6.7	25		185						148		40	48			2490
9-1-70		6.8	80														
2		6.4	30		152						134		31	48			2230
3		6.6	25														
4		6.9	50		351						130		157	165			4150
5		6.8	50														
6		6.5	40														
7		8.3	210														
8		6.9	40		384						284		142	128			5300
9		6.6	45		468						167		11	12			5380
10		6.8	50														
11		6.9	60		535						237		136	196			6060
12		7.1	80														
13		7.1	85														
14		7.2	100		556						330		212	225			8050
15		7.4	120														
16		7.1	115		620						421		181	209			7830
17		7.0	100														
18		6.9	80		612						384		147	225			
19		7.0	90														
20		6.9	75														
21		6.8	75		672						398		215	235			7560
22		7.1	100														
23					681						347		203	265			7430
24		7.0	75														
25		7.0	80		668						428		147	220			7880
26		7.2	90														
27		6.7	55														
28		6.7	65		637						213		212	280			6490
29		7.4	120														
30		6.8	60		552						104		303	272			5260
10-1-70		6.9	75														
2		7.0	75		620						90		316	245			5500
3		7.1	90														
4		7.0	75														
5		6.6	45		712						322		286	223			7430
6		6.8	60														
7		6.5	60		603						302		263	213			6560
8		6.6	65														
9		6.8	65		500						230		162	183			5420
10		6.9	65														
11		6.5	35														
12		6.7	45		471						126		313	234			5230
13		6.7	45														
14		6.7	45		517						123		348	253			5940
15		6.5	65														
16		6.8	45		512						92		339	275			6130
17		6.8	50														
18		6.8	55														
19		6.8	75														
20		6.7	135														
21		8.7	200		510						.76		392	377			6180
22		10.1	430														
23		6.5	45		381						22		70	210			5270
24		6.8	65														
25		6.7	60														
26		6.8	75		719						145		551	431			8510
27		6.7	50														
28		6.5	50		396						220		384	159			5330
29		6.7	50														
30		7.3	215		480						2.3		203	168			5150
31		7.3	125														
11-1-70		6.8	65														
2		6.7	60		524						154		279	287			6530
3		9.7	975														

APPENDIX A-3: page 5 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
11-4-70		8.8	580		280						284		84	0.08			5150
5		8.6	405														
6		8.2	250		227						382		77	0.01			4720
7		7.6	110														
8		6.7	50														
9		6.8	50		265						568		44	<0.01			6490
10		7.1	105														
11		6.9	55		332						588		54	0.05			6690
12		6.9	60														
13		7.0	60		319						381		72	0.13			6340
14		6.8	45														
15		6.8	40														
16		7.0	65		301						465		98	0.31			6270
17		7.0	55														
18		6.7	45		275						339		79	0.03			5440
19		6.7	45														
20		6.7	40		266						185		105	0.02			4270
21		6.9	60														
22		6.9	60														
23		7.0	75		562						30		197	<0.01			4440
24		7.5	180														
25		6.8	40		245						129		81	<0.0			3700
26		6.7	30														
27		6.5	525		422						137		165	0.01			4150
28		6.4	30														
29		6.6	40														
30		6.9	75		470						20		213	211			5170
12-1-70		6.8	50														
2		6.8	45		409						48		224	250			4910
3		6.9	730														
4		6.9	55		405						73		170	250			5140
5		6.8	45														
6		6.7	55														
7		6.8	60		408						96		260	260			5720
8		6.6	50														
9		6.6	45		438						157		161	279			6100
10		7.0	70														
11		7.0	75		511						24		233	225			5230
12		7.5	300														
13		6.7	70														
14		6.9	60		406						56		213	200			4400
15		6.9	80														
16		6.8	60		404						148		167	205			4950
17																	
18		8.5	520		375						.82		125	130			3380
19		6.7	35														
20		6.9	70														
21		6.6	40		328						312		109	110			5340
22		6.7	40														
23		6.7	50		375						255		158	180			5850
24		6.9	70														
25		6.8	60		417						78		238	196			5600
26		6.9	60														
27		6.8	50														
28		6.9	60		460						66		210	190			5350
29		7.0	55														
30		7.0	85		477						7.4		282	255			5490
31		7.2	160														
1-1-71		6.9	55		383						97		209	175			5600
2		6.7	60														
3		6.7	50														
4		6.6	65		534						129		260	257			7460
5		6.9	85														
6		7.1	115		479						185		224	195			7370
7		6.7	50														
8		7.2	130		384						211		171	85			6360
9		8.1	250														
10		8.0	205														
11		7.4	80		384						260		85	30			7080

APPENDIX A-3: page 6 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
1-12-70		6.8	45														
13		6.9	55		303						594		81	71			7200
14		7.5	470														
15		7.0	65		329						552		193	116			7030
16		7.0	75														
17		7.1	70														
18		6.8	55		337						454		160	125			6120
19																	
20					362						417		160	139			6410

APPENDIX A-4: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES ANALYTICAL DATA FOR EFFLUENT FROM THE DENITRIFICATION UNIT

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
2-1-70		6.4	119														
2		6.4	102	159							188	45	48	44			2900
3		6.5	134														
4		7.3	190	196							179		14	15			2650
5		7.1	174														
6		6.9	166	96							155		11	10			2620
7		7.0	111														
8		7.0	190														
9		7.0	205	29							193	29	0.1	0.05			2860
10		7.5	205														
11		7.5	205	29							213		4.7	2.8			2820
12		7.4	213														
13		6.7	237	30							220		1.1	0.2			2830
14		7.4	316														
15		7.4	270														
16		7.3	261	37							169	43	11	7.8			2230
17		6.5	125														
18		6.4	100	40							147		69	59			2370
19		6.4	100														
20		6.7	110	30							186		56	51			2410
21		6.6	235														
22		7.2	270														
23		7.1	230	31							157	28	24	13			2140
24		6.6	240														
25		7.4	280	24							126		14	8			2220
26		7.0	275														
27		7.1	240	24							151		19	16			2510
28		7.3	305														
3-1-70		7.4	235														
2		7.3	300	28							142	24	1.2	0.01			2610
3																	
4		7.6	230	16							116		28	22			2330
5		7.0	225														
6		7.8	320	14							56		16	10			1800
7		8.0	360														
8		8.3	420														
9		8.0	435	24							74	26	2.1	2.7			2270
10		8.0	410														
11		8.3	435	15					12		102		1.1	1.0		468	2430
12		7.8	420														
13		7.3	200	24					8		131		52	48		468	2615
14		6.9	170														
15		6.7	300														
16		7.2	370	45	418	193			8		153	34	1.1	0.01		498	2560
17		7.0	350														
18		6.5	350	37							197		1.4	0.01			2970
19		7.3	355														
20		7.4	350	43							134		1.4	0.16			2410
21		7.3	425														
22		7.9	355														
23		7.0	355	28							227	26	1.4	0.11			3070
24		7.2	395														
25		6.9	375	36							224		1.7	0.02			3110
26		7.0	410														
27		6.9	385	43							176		1.7	0.02			2830
28		6.7	400														
29		7.1	505														
30		6.4	435	84							179	35	0.5	0.05			3070
31		6.5	440														
4-1-70		7.0	580	40							265		1.0	0.01			3600
2		7.4	600														
3		7.4	570	46							322		0.6	0.01			4000
4		7.8															
5		7.8	410														
6		8.1	480	28	470	105					147	28	52	53	24		3550
7		7.7	385														
8		7.7	430	20							90		38	29			2650
9		7.7	275														
10		8.0	300	16							71		24	35			2540

APPENDIX A-4: page 2 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl-	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
4-11-70																	
12																	
13		8.7	475	65							112	28	35	43			3440
14		8.3	320														
15		8.1	460	44							189		0.1	0.05			3570
16		8.5	415														
17		8.5	385	30							139		82	11			4700
18		8.3	400														
19		8.0	290														
20		7.6	220	44							391	28	141	169			7230
21		8.3	460														
22		8.0	375	68							626		124	124			9000
23		8.1	420														
24		8.0	425	290							882		66	85			10300
25		8.0	375														
26		8.2	500														
27		7.9	375	102							980	62	58	92			10180
28		7.2	75														
29		8.0	385	129							875		189	229			11100
30		8.0	340														
5-1-70		8.0	360	110							595		339	293			10810
2		8.2	450														
3		7.9	425														
4		7.6	450	41	1000	141					525	70	328	405	16		11800
5		8.0	475														
6		8.9	935	40							616		376	357			11200
7		8.8	1100														
8		8.4	850	159							1170		22	16			12500
9		8.4	790														
10		8.2	550														
11		7.9	325	82							812	43	0.1	0			7920
12		7.9	285														
13		7.9	300	55							343		0.1	0.02			4210
14		8.1	400														
15		8.6	775	44							966		0.1	0.01			9560
16		8.2	540														
17		7.8	460														
18		7.9	480	166							1550	59	0.1	0.01			13100
19		7.8	465														
20		7.5	370	65							1210		0.1	0.02			10500
21		7.4	335														
22		7.6	315	15							490		0.1	0.01			5240
23		7.4	315														
24		7.0	180														
25		6.7	100	32							273	49	44	93			4000
26		6.8	150														
27		8.4	675	23							371		8.1	9.1			5070
28		7.8	550														
29		7.7	550	53							1190		0.4	0.01			10700
30		7.9	550														
31		7.7	450														
6-1-70		7.7	450	53	1590	734					1610	78	0.1	0.03	36		14000
2		7.1	280														
3		6.9	190	50							812		0.1	0.03			7130
4		7.3	260														
5		7.3	240	67							469		0.2	0.03			4710
6		7.1	210														
7		7.1	220														
8		7.0	205	61							196	14	0.1	0.05			2480
9		7.1	230														
10		7.3	260	60							160		0.2	0.06			2270
11		7.4	290														
12		7.5	310	76							176		0.2	0.02			2340
13		7.8	380														
14		7.9	375														
15		8.3	450	75							82	20	0.1	0.02			2190
16		7.8	340														
17		7.1	220	20	520						90		51	40			2700
18		8.1	275														

APPENDIX A-4: page 3 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
6-19-70		8.5	425	73	313						190		3	2.8			3800
20		8.8	500														
21		8.9	575														
22		8.6	430	32	184						133	26	45	47			3930
23		8.7	560														
24		8.7	525	13	515						202		158	14			4320
25		8.6	570														
26		8.5	380	7	367						94		96	120			4480
27		8.5	400														
28		8.8	560														
29		8.5	450	10	390						132	27	48	52			4540
30		9.0	620														
7-1-70		9.0	600	26	487						92		129	130			5320
2		9.3	525														
3		9.0	875	35	504						164		0.3	0.02			
4		8.4	480														
5		7.9	300														
6		7.5	280		565						265	30	0.2	0.03	33		3760
7		8.3	450														
8		8.3	400		409	266					228		20	24			4330
9		8.6	565														
10		8.5	520		469						216		3.8	4.4			4360
11		8.6	540														
12		8.6	540														
13		8.4	475		464						204	30	7.2	7.3			4140
14		8.8	515														
15		8.6	450		392						190		35	31			4400
16		8.4	385														
17		8.5	520		466						281		2.0	3.4			49300
18		8.8	745														
19		8.3	375														
20		8.2	385		437						330	34	0.3	0.01			4670
21		8.5	475														
22		8.4	460		410						308		16	19			5180
23		8.2	500														
24		8.2	515		504						759		0.1	0.01			8910
25		8.1	460														
26		7.9	370														
27																	
28		6.9	270														
29		6.7	245	292	1400						1170		0.2	0.01			10800
30		7.3	250														
31		6.6	250		1140						750		0.4	0.06			7540
8-1-70		7.0	225														
2		7.0	210														
3		7.2	235		494	189					174	21	0.2	0.01	39		2600
4		7.5	280														
5		7.5	340		573						146		0.1	0.01			2390
6		8.0	415														
7		7.6	315		262						148		0.3	0.47			2360
8		7.9	285														
9		7.7	305														
10		7.8	345		360						182	22	0.1	0.02			2570
11		7.8	375														
12		7.8	360		292						171		0.3	0.09			2580
13		7.5	260														
14		6.9	240		596						78		0.1	0.05			1760
15		7.2	155														
16		7.6	210														
17		7.8	280		322						113	16	0.5	0.01			2030
18		7.8	295														
19		6.5	40		67						124		40	43			2150
20		6.9	50														
21		8.2	435	150	933						85		0.3	0.01			2200
22		8.2	405														
23		8.1	350														
24		7.6	325		743						209	24	0.1	0.01			2980
25		7.3	310														
26		7.6	350		691						258		0.2	0.08			3500

APPENDIX A-4: page 4 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
8-27-70		7.3	295														
28		7.4	290		629						479		0.2	0.18			5050
29		7.4	300														
30		7.3	305														
31		7.7	390		544						255	25	0.2	0.03			3280
9-1-70		9.0	675														
2		8.0	350		456						112		0.2	0.08			2060
3		8.2	500														
4		8.6	475		468						119		17	21			3320
5		8.5	550														
6		7.7	925														
7		8.5	590														
8		6.8	760		563						254	33	0.2	0.15			4230
9		8.6	665		605						167		11	12			4490
10		8.5	675														
11		8.5	710		684						208		15	18			5020
12		8.5	800														
13		8.5	875														
14		8.5	775		558	136					296	43	0.4	0.04	10		5720
15		8.4	740														
16		8.4	700		657						386		2.9	2.9			6520
17		8.3	750														
18		8.2	580		596						378		18	31			6520
19		8.3	640														
20		8.4	725														
21		8.3	675		1350						367	172	17	18			6580
22		8.3	715														
23					605						367		40	44			6750
24		8.4	660														
25		8.2	575		668						414		57	75			7320
26		8.3	550														
27		8.5	640														
28		8.5	625		691						207	40	67	79			5990
29		8.5	650														
30		8.7	700		626						137		99	58			5100
10-1-70		8.9	750														
2		9.0	710		788						64		80	66			4540
3		9.2	780														
4		9.0	830														
5		8.7	725		931						202	375	115	64	12		5630
6		8.6	775														
7		8.2	650		690						258		114	74			6070
8		8.3	650														
9		8.4	640		587						252		22	8			5150
10		8.4	700														
11		8.0	700														
12		8.5	780		683						204	60	3	2			4720
13		8.8	830														
14		8.9	960		1750						148		45	24			5300
15		8.9	1045														
16		9.0	950		1130						116		78	46			5780
17		9.0	930														
18		9.1	1000														
19		9.1	980														
20		9.2	925														
21		9.2	835		792						55		131	126			5880
22		9.5	920														
23		9.2	1175		1130						120		8	11			5270
24		8.8	1000														
25		9.1	1035														
26		9.1	1435		1015						190	42	1.4	0.07			6440
27		9.1	1225														
28		8.9	900		587						207		11	1.18			5600
29		8.9	775														
30		9.0	900		926						1.1		33	38			4480
31		9.4	1020														
11-1-70		9.0	1005														
2		9.0	950		974	362					160	97	15	17	11		5590
3		9.5	1200														

APPENDIX A-4: page 5 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRATE	NITRITE			
11-4-70		8.8	1130		1160						246		0.6	0.01			5790
5		7.8	655														
6		7.0	420		1350						386		0.5	0.01			5100
7		7.0	280														
8		6.9	250														
9		7.0	300		864						599	50	0.2	<0.01			6460
10		7.1	350														
11		7.6	410		1000						596		0.2	<0.01			6690
12		7.5	420														
13		7.6	470		1020						515		0.3	<0.01			6340
14		7.8	495														
15		7.2	470														
16		7.5	525		1090						465	18	0.3	0.01			6200
17		7.3	520														
18		7.7	525		935						440		0.2	<0.01			5640
19		8.0	575														
20		8.0	560		675						249		0.4	<0.01			4430
21		8.1	550														
22		8.5	675														
23		8.8	675		624						87	43	19	<0.01			4240
24		8.7	550														
25		8.1	395		613						98		66	.07			3880
26		8.5	480														
27		8.1	525		456						157		9.6	<0.01			3800
28		8.5	490														
29		8.6	560														
30		8.9	700		500						78	31	24	28			4330
12-1-70		9.0	660														
2		9.1	680		546						62		62	85			4680
3		9.2	730														
4		9.1	705		501						81		58	57			4620
5		9.1	930														
6		9.2	915														
7		9.0	930		672	245					136	34	1.1	.03	7.2		5150
8		9.0	860														
9		8.9	840		556						185		36	30			5550
10		9.1	775														
11		9.4	825		560						46		45	57			4710
12		8.8	990														
13		9.5	900														
14		9.3	820		575						102	32	.2	.03			4120
15		9.2	840														
16		8.8	840		594						99		.2	.12			4230
17																	
18		7.6	830		863						2.2		.4	<0.05			3210
19		7.6	650														
20		8.0	575														
21		8.2	575		755						241	41	.4	.02			4540
22		8.3	575														
23		8.5	680		582						249		.4	.06			4840
24		8.8	850														
25		9.0	880		755						73		.1	.06			4800
26		9.0	860														
27		8.9	780														
28		8.8	700		575						64	84	39	45			4730
29		9.0	710														
30		9.4	850		544						4.6		42	33			4690
31		9.4	1025														
1-1-70		8.7	535		600						86		54	60			4600
2		8.7	760														
3		8.6	775														
4		8.6	875		773	276					118	160	2.1	.02	5.2		5600
5		8.8	950														
6		8.7	840		707						176		18	17			6290
7		8.4	740														
8		7.6	500		706						210		.4	.02			6050
9		7.8	425														
10		7.8	380														
11		7.9	330		508						594	34	4.0	3.0			6580

APPENDIX A-4: page 6 of 6

DATE	TEMPERATURE °F	pH	ALKALINITY, mg/l $CaCO_3$	ORGANIC CARBON mg/l C	OXYGEN DEMAND, mg/l O_2		PHENOLICS, mg/l C_6H_5OH	CYANIDE, mg/l CN	THIOCYANATE, mg/l SCN	SULFIDE, mg/l S	NITROGENOUS COMPONENTS, mg/l N				PHOSPHATE, mg/l PO_4	CHLORIDE, mg/l Cl	CONDUCTIVITY, micromhos/cm
					CHEMICAL	BIOCHEMICAL 5-day					AMMONIA	ORGANIC NITROGEN	NITRITE	NITRATE			
1-12-71		6.8	250														
13		7.3	375		786						605		.3	.24			6840
14		7.5	470														
15		7.8	600		743						529		.3	.02			6800
16		8.0	640														
17		8.1	525														
18		8.2	625		641						440	36	.3	.04			
19																	
20					590						403		.3	.32			6160

APPENDIX B-1: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES
ANALYTICAL AND OPERATIONAL DATA FOR THE CARBONACEOUS UNIT

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature, °F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
2-1-70								0.85	92	0.2										Sludge recycle 1 gpm.
2									74	0.6										
3									90	0.2										
4									65	0.4					3					Flow off over 1 hr.
5									79											
6									75	1.1				9 1/4	2.5					
7									71					7 1/2						
8									80					7 1/2						
9									79	3.25				7	11.0					
10									74					8						
11									88	8.5				9	13.0					
12									74	8.5				7	40.0					
13									74	6.0					24.0					
14							0.075		80	7.5				7	2.0					
15									83	10.0				7	25.0					
16									73	9.5				6	17.0					
17									83					6						
18									81	9.0				6 1/2	25.5					
19									78					7 1/2						
20									82	12.0				6	26.0					
21									72					6 3/4						
22									78	15.0				7	40.0					
23									79	18.0				7 1/2	40.0					
24									79					7 1/2						Aerator off 1 hr.
25									80	20.0			2	6 1/2	40.0					2% blowdown to continue on daily basis
26									78					7 1/2						
27									81	23.0				10 1/2	40.0					
28									83					8 1/2						
3-1-70									85					9						
2									78	28.0				9 1/2	50.0					
3																				
4									87	26.0				10	19.0					
5									86					14						
6									77	30.0				12	90.0					
7									82					12 1/2						
8									80					8 1/2						
9									81	45.0				11	105.0					
10									83					14						
11									83	50.0				9 1/2	127.0					

APPENDIX B-1: page 2 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature, °F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
3-12-70									77											
13									72	73.0					140.0					
14									82					13						Low waste flow.
15									75					8						
16							0.2	0.8	82	69.0				7 1/2	36.0					
17			1						80					8 1/2						
18			1						76	18.0				9	163.0					
19			1						86					10						
20						1			74	60.0				8	107.0					Clarifier drive motor off ? hrs.
21									67											No sludge recycle.
22									75					4						Sludge recycle 3/4 gpm.
23									82	61.0				5	166.0					Waste flow off ? hrs.
24						1			80				4	6 1/2					X	
25						1			84	65.0			4	8	218.0				Y	Waste flow off
26									79				6	6						
27									79	85.0			6	7	130.0				X	
28					2	2			82				4	6					X	
29						2			78				6	5						
30							0.25		80	56.0			6	4 1/2	137.0				X	
31									82				6	5					X	
4-1-70					1/2				82	'7.0			6	5	135.0				X	
2	750								75				2	4					X	
3						2			80	85.0			6	5	130.0				X	
4						2			75					3			X		X	
5						1			123				4	4			X			Temp. problem; leaking steam valve.
6									76	30.0			2	7	35.0					
7									75	25.0										Sludge now lighter in color.
8									75	25.0				5 1/2	25.0		X			
9		30							79	24.0							X			
10									82	28.0				5	50.0		X			
11																				
12																				
13									80	50.0				4	48.0					
14									80					3						
15		50							79	26.0				6	42.0					Waste flow off ? hrs.
16									83	25.0				4 1/2						
17									83	50.0				3 1/2	145.0					Recycle pumps off ? hrs.
18									83	89.0				3						
19									82					3 1/2						

APPENDIX B-1: page 3 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature,°F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
4-20-70							0.40	0.60	79	120.0			2	3 1/2	262.0					Reestablished 2% daily blowdown.
21									81					3			X		X	
22									85	200.0				3	412.0		X			
23									85					3			X			
24									85	185.0				3 1/2	740.0		X			Sludge recycle, 0.9 gpm.
25		100							85					4			X			
26									85					3						Waste flow off,
27									85	200.0	1300			4	400.0		X			
28									85					3			X			
29									87	165.0	1100			4						
30		125							87											
5-1-70									80	200.0	1060			3	400.0		X			
2									70					3			X			
3							0.36		75					3						
4		125							75	175.0	1300			2 1/2	250.0		X			
5							0.55	0.45	76					3 1/2						Waste flow off ? hrs.
6									79	165.0	1300			3	325.0					
7									79					2 1/2						Out of T.B.P.
8									80	160.0	1170			4	600.0					
9									84								X			
10									85					3						
11									85	250.0	1200			3	600.0					
12									88					4 1/2						
13									87	213.0	1500			4	623.0					
14									86					5 1/2			X		X	
15									86	250.0	1320			4 1/2	725.0					
16									80			3.1		6						
17									76					3						
18									80	325.0	1200			3						
19							0.70	0.30	85			2.25		3						
20									86	200.0	1400	3.1		4	785.0		X			Power off, 40 min.; Emergency air on.
21									84			4.0		2 1/2						Waste flow off,10 hrs.
22		50							84	175.0	1100	4.8		3	300.0					
23	750	100							86	250.0		3.0	2	3 1/2						
24									84				2							
25									85	175.0			2	3	400.0					
26	750	125							88	160.0		4.1		4						
27	750	125					0.5		87	200.0					350.0					Waste flow only, 0.5 gpm.

APPENDIX B-1: page 4 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature,°F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
5-28-70							0.65		87	150.0		3.0								
29							0.60	0.45	86	175.0		3.1		3	365.0					
30	560	100					0.70	0.30	87	175.0		3.0		4					X	
31	750	125							84	214.0		2.1		4 1/2			X			
6-1-70											1020									
2	750	150							82	140.0		2.25		2 1/2			X			
3									80	130.0	930			2 1/2	335.0					Waste feed off, ? hrs.
4	0	0							80	160.0				2						
5									88	180.0	980			2	214.0					System off 2 hrs.
6	750	150							82					3						System off 1 1/2 hrs.
7									87	100.0				3			X			
8	750	150							86	100.0			6	1 1/2	175.0					
9	600	125							87				6	1 1/2						
10	530	125							87	80.0			6	1 1/2	118.0					
11	490	98							89	75.0			6	1						
12	510	75							89	70.0			6		150.0					
13	490	100							90	60.0			6							
14									92	150.0			2	3			X		X	
15	750	50							91	75.0			2	3	100.0					
16							0.75	0.15	91	43.0			2	1 1/2						Waste feed off, 4 hrs.
17	750						0.50	0.50	90	42.0		0.2	2	2	50.0					Discovered low aeration rate.
18									88	50.0		2.4	2	1 1/2	100.0		X			
19									87	58.0		2.7	2	3 1/2	100.0				X	W.A.L. Storage tank now being filled slowly.
20	750								89			2.7	2	2					X	
21									88				2	2						
22	0								90	40.0			2	2	100.0					
23	750								90	42.0		2.0	2	2						
24									87	57.0		1.5	2	2	100.0					Waste feed off, 2-3 hrs.
25	750	100							88			3.1	2	3			X			
26									88	37.0		1.4	2	2 1/2	66.0					
27	750	100							90			1.8	2	3					X	
28									89				2	3					X	
29									91	50.0		2.3	2	3	135.0					
30									91			1.3	2	3						
7-1-70	750	100							87	60.0		2.	2	3	85.0					
2									88			1.8	2	3						
3	750	100							90	50.0			2	3	100.0					
4									90				2	3						

APPENDIX B-1: page 5 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature, °F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
7-5-70									88				2	3						
6	750	100							87	7.0		3.0	2	3	50.0					
7									88			1.8	2	2 1/2						
8	750	100							93	40.0		2.0	2	2	125.0				X	
9									88			1.9	2	3					X	
10	750	100							91	44.0		2.0	2	3	100.0					
11									90			2.6	2	3						
12									89			2.3	2	3						
13	750	100							88	75.0		2.7	2		100.0					
14									85			2.7	2	3						
15	750	100							87	50.0		2.0	2	3	33.0					
16									88				2	2 1/2						Waste feed off 2 hrs.
17									88	65.0		2.1	2	3	125.0					
18	750	100							88				2	3						
19									88				2	3						
20	750	100					0.60	0.40	88	75.0		2.5	2	3	125.0					
21									89			2.4	2	3					X	
22							0.70	0.30	85	92.0		2.6	0	2	100.0					
23	750	150							82			0.1		3						
24	750	100							89	75.0		2.2		2	260.0		X			
25	750	100							90			2.0		3			X			
26									87			1.5		3			X			
27																				
28	750	150							90			1.9		2						Waste feed off, 2 hrs.
29							0.70		89	155.0				3 1/2	300.0					Waste feed off, ? hrs.
30									87			2.3		2 1/2			X		X	
31									88	150.0		1.8	2	4	150.0					
8-1-70									90			0.8	2	4					X	
2	750	150							91			2.3	2	5						
3									92	125.0		2.4	2	4	185.0					
4	750	150							92			1.4	2		250.0		X			
5									91	125.0			2							
6	750	150					0.55	0.29	88			1.9	2	4						
7									88	100.0			2	3	200.0					
8							0.58		91				2	2						Sludge recycle rate; 1 gpm.
9	750	150					0.63	0.27	90				2	3						
10							0.55	0.28	89	120.0			2	3	275.0					Sludge recycle rate, .85 gpm.
11	750	150					0.44	0.29	97				2	3						Sludge recycle rate, .67 gpm.
12								0.64	88	150.0				2 1/2	300.0					

APPENDIX B-1: page 6 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature,°F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
8-13-70							0.67	0.50	89					2 1/2						
14	750	150					0.56	0.25	85	150.0			2	3	250.0					
15							0.50	0.25	89				2	3						
16							0.58	0.29	90			2.1	2	3						
17	750	150					0.53	0.26	88	120.0		2.5	2	3	123.0					
18							0.70	0.31	89			.5	2	3						System off, 1 1/2 hrs.
19	750	150							86	70.0		1.8		2 1/2	170.0					Waste feed off,
20									92					2 1/2						Reduced aerator volume; on 70% waste.
21							0.64	0.16	88	150.0		1.2		2	209.0					Waste feed off, ? hrs.
22	750	150					0.60	0.27	90			1.3		2						
23							0.64	0.28	90			0.9		2						Waste feed off, ? hrs.
24	750	150					0.64	0.28	90	54.0		0.7		2	250.0					
25									88	15.3			0.1		200.0					Waste feed off, ? hrs.
26	750	100							85	130.0			0.1	2	218.0					Waste feed 70%.
27									82			3.0	0.1	1 1/2						
28	750	100							86	150.0		2.0	1.0	2	200.0					
29									87			2.4	1.0	2						
30							0.53	0.25	85			1.5		2						Waste feed off ? hrs.
31	750	150					0.53	0.25	87	125.0		1.3		2						
9-1-70									86			1.3	0.5	2						
2	750	100							86	200.0			0.5	2	233.0		X			
3									90			1.0		1 1/2						
4	750	150							90	160.0	1420	1.0	1	3	200.0		X			
5									90			1.5	1	2			X			
6									91				1	1						Waste feed off ? hrs.
7							0.50	0.21	90	150.0		1.1		2	327.0		X			Waste feed off ? hrs.
8	750	150							90				1	3			X			
9									89	200.0		1.6		1 1/2	407.0		X			Waste feed off ? hrs.
10									92			0.57	2	1 1/2			X	X		Ammonia odor over aerator.
11	750	150							91	150.0		0.3	1	3	250.0		X	X		
12									90			1.4	1	3						
13	750	150							90				1	2						Waste feed off 1 hr.
14									90	135.0	1220	1.0	1	2	180.0					
15	750	200							93			0.86	2	1			X			
16									89	122.0		1.7	2	1	210.0					
17	750	200							93				2	1						Much less foam.
18									90	150.0		1.3	.5	2	180.0					
19									90			1.0	.5	2						
20	750	200							92	0		1.4	.5	2						Waste feed off, 45 min.

APPENDIX B-1: page 7 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature, °F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
9-21-70	750	200							92			1.4	.5	2						Waste Feed Off, 45 min.
22	750	200							89				.5	2						
23																				Daily data sheet missing.
24									87				2	2						
25	750	200							90		640		.5	2	125.0					
26									89				.5	2						
27	750	150							84				.5	2						
28									78	100.0	760		.5		150.0					
29									75					2			X			
30	750	200							80	65.0				1						Waste feed off ? hrs.
10-1-70									78					1			X			
2	750	200							83	30.0				2	11.0		X			
3									84			0.7		2						
4									87			0.8								
5	750	200							88	21.0		1.0		2	41.0					
6	750	200							90					1						Waste feed from 70% to 50%.
7									87	8.0		0.9		1	16.0					Effluent, very dark color.
8									88	7.0				2						Waste feed from 50% to 25.
9									68	14.0					6.0					
10	750	100							72											
11									78			6.0		2						
12									78	4.0		1.9		2	1.0					
13									78			1.9		2						
14									77	0.6					0.1					
15									78					2						Waste feed from 25% to 15%; reseeded system.
16									75	3.0		2.0		1 1/2	0.1					
17									74					2						
18									74			2.6		2						
19									75	1.0				2	0.5					
20	750	100							75	4.0				2 1/2						
21									75	3.5		2.4			0.5					
22									79	4.0		2.4								
23									81	1.2				2	1.5					
24									78					2						
25									80	1.5				2						
26									92	2.5				2	2.5					
27									86	10.0		3.7		2 1/2	7.5			X		
28	750	150							78	13.0		2.8		2	6.5		X			Solids lighter color, waste feed now 40%.

APPENDIX B-1: page 8 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature, °F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
29									71	10.5		1.3		2			X			
30									71	20.0	280	2.4		2	15.0					
31	750	150							70					2 1/2						
11-1-70									75			2.3		1 3/4						
2									73	15.5	220	2.5		2 1/2	20.0					Waste flow off ? hrs.
3									67	15.0		6.6		3	22.0		X			Waste feed now 50%.
4	750	150							67	10.5		2.6		2 1/2	21.0					
5	750	150							64	11.0		3.3		2						Waste flow off ? hrs.
6									69			2.7		2						
7									75			1.6		2						
8									80					2						
9	750	150							78	15.0		2.2			10.0					
10								0	72			1.8		1 1/2						No dilution water, ? hrs.
11									73	4.5		1.94		1 1/2	15.0					
12	750	150							73	4.5				2	9.0					
13									78	4.0				2	3.0					
14									71					1 1/2				X		
15	750	150							67			1.2		2						
16									61	1.7		3.0		2	1.6					
17									69	1.5		2.6		2						Waste feed reduced to 20%.
18	750	150							75	1.3		2.4		2	1.0					
19									75	1.5		2.0		3						
20									75	1.0	100	2.7		3	15.0					
21									74	1.0		2.8		3 1/2	1.0					
22									78			2.5		3			X			
23									72	1.0					1.0					
24									62			4.3		4						
25	750	150							65			1.4		3	1.1					
26									75	1.3		2.9		3						
27									78	2.5	140			4	3.0					
28									79	3.5		2.6		4	10.5					
29									80	3.5		2.6		4	5.5					
30									79	4.0		2.6		4	5.0					
12-1-70	750	150							80	10.0		2.4		4	5.0					
2									91	12.0		2.3		3 1/2	11.0					Waste feed now 35% - Temp. 90°.
3									90	75.0		2.0		9	80.0		X			
4									89	75.0				3	130.0					
5									90	65.0		3.1		4						
6	750	150							90			3.1		3						

APPENDIX B-1: page 9 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature,°F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
12-7-70									87	45.0		3.3		3	78					
8									88	115.0		4.1		4 1/2	150.0					
9									88	125.0		4.1		3 1/2	250.0		X			Waste feed now 50%.
10									87	115.0				3 1/2	275.0		X	X		
11									91	280.0		1.6		3 1/2	425.0		X			
12									92			2.3		3 1/2						
13									91	150.0		1.8		3	250.0		X			
14									91	180.0	640			3	250.0					
15									89	275.0	1060	2.4		2 1/2	540.0					
16	750	150							92	150.0		2.6		2 1/2	450.0					
17																				
18	750	150							86	150.0		.86		3	400.0					Waste feed off, ? hrs.
19									85	200.0		2.0		3	300.0					
20									85	200.0		1.9		3	400.0			X		
21									84	200.0		2.3		3 1/2	225.0			X		Waste feed off, ? hrs.
22	750	150							82	180.0		2.3		3 1/2	350.0					
23									84	200.0		1.8		3	400.0					
24									90	200.0				3	350.0					
25	750	150							88	200.0		1.8		3	375.0					
26									93	225.0		2.3		3	350.0					
27									90			1.8		3						
28									86	225.0		1.7		3	450.0					
29	750	150							83	250.0		2.3		3	450.0					
30									88	280.0		1.8		3	350.0					
31	750	150							88	250.0		1.9			450.0					
1-1-71									88	220.0				3	440.0					Waste feed now 25%.
2									87	270.0		2.4		2 1/2	430.0					
3									86	350.0				3						Waste feed off, ? hrs.
4	750								90	280.0				2 1/2	593.0					
5									95	300.0										Waste feed now 35%.
6									97	250.0		1.7		3	450.0					Waste feed off,
7	750								95					2						Waste feed off,
8									95	350.0				2	425.0					Waste feed now 50%.
9	750	150							96			1.9		3						
10									87			3.1		2						Waste feed off,
11									85	275.0				2	408.0					Waste feed reduced intermittently.
12									84					2						
13	750	150							85	250.0				2	725.0		X			
14									86					2				X		

APPENDIX B-1: page 10 of 10

DATE	CHEMICAL ADDITIVES						BIOLOGICAL REACTOR							Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	TO EXCESS AMMONIA LIQUOR ml/1500 gal.		TO BIOLOGICAL REACTOR, pounds/day				INFLUENT FLOW RATES gals./min.		MIXED LIQUOR											
	Phosphoric Acid	Tributyl-Phosphate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Excess Ammoniacal Liquor	Dilution Water	Temperature,°F	Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Dissolved Oxygen mg/liter O_2	Blowdown, percent/day		Imhoff Cone, ml/liter	Suspended Solids, mg/liter	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
1-15-71									86	250.0				2 1/2	450.0					
16									90					3						
17	750	150							89					2						
18									89	270.0				2	490.0					

APPENDIX B-2: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES
Analytical and Operational Data for the Nitrification Unit

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
2-1-70	1												90	6.6	119		10.0								Sludge recycle 1 gpm.
2				1									78	7.0	102		4.0								
3													72	6.7	53		3.0								
4													75	7.2	95		2.5			0.75					Reactor off 45 min.
5													92				5.0								
6													85	6.8	55		4.5		4	7.0					
7				2	1								80	7.7	150				4 1/4						
8				2	1								84	7.5	126				3 1/2						
9				1	1/2								81	6.9	86		4.0		3	11.0					
10					1								77	6.9	111				4						
11				1	1/2								80	6.7	123		10.0		4	12.0					
12				3	1								83	6.6	127		5.5		3 1/2	8.0					Attempting to maintain Ph8,alk. 200
13				2	1								77				5.0			10.1					
14					1 1/2								82	7.3	205		5.0		3	---					
15				2	2 1/2								85	7.2	178		3.5		3 1/2	10.0					Sludge return problem
16				2	2 1/2								76	7.3	174		5.5		3 1/2	17.0					
17					2								78	7.4	138				4						
18					2								81	6.9	135		4.9		3 1/2	15.0					
19					2								84	7.2	166		5.0		4 1/2						Rising sludge noted during Imhoff cone test
20					2								82	9.6	130		6.0		4	13.0					
21					2								80	6.8	125				3 1/2						
22					4								80	6.9	140		7.5		4 1/2	19.0					
23					4								73	7.1	115		9.0		5 1/2	25.0					
24					4								82	6.8	120				6						Mixer and air off, ? hrs.
25					4								90	7.0	170		9.0		4 1/2	22.0					
26						3							80	7.2	174				4 1/2						
27						3							82	6.4	90		8.5		5	15.0					

APPENDIX B-2: page 2 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
28							3						85	7.1	123				6						
3-1							4						87	7.0	117				5 1/2						
2							6						84	6.9	103		8.0		6	18.0					
3							4																		
4							6						87	6.8	75		7.5		6	40.0					
5							6 1/2						84	7.3	160				8						
6							3						84	7.5	162		7.0		8 1/2	24.0					
7						1 1/2	4 1/2						82	7.6	193				10						
8						1 1/2	5						80	7.2	154				8						
9						2 1/2	5 1/2						81	7.1	165		8.0		9	23.0					
10						4 1/2	2 1/2						84	7.2	153				10						
11						1 1/2	3						84	7.7	166		9.0		7	23.0					
12						2 1/4	2						78	7.0	120										
13						3 1/2	1/2						74	7.1	110		9.0		8	20.0					
14						3							79	7.2	105				9						
15						3	1						80	7.5	158				7						
16						2 1/2	1/2						83	7.5	147		16.0		9	36.0					
17						3	1/2						82	6.7	108				10 1/2						
18						3	1/2						79	6.6	118		18.0		10	52.0					
19				1/2		3	1						88	6.9	98				9 1/2						
20						3 1/2	1/2						80	7.0	127		15.0		8	33.0					
21						2							80	7.1	145										
22						3	1/2						70	7.8	162				4 1/2						
23						2	1 1/2						83	7.3	150		21.0		6	44.0					
24						3	1/2						83	70	103				7						
25						3	2 1/2						87	7.2	113		24.0		7	45.0					
26				1/2			3 1/2						81	7.0	92				5						Recycle pump off, ? hrs.
27						3	1 1/2						81	6.9	93		2.0		6	43.0					
28						2	1/2						86	7.2	145				6						
29						3	1						81	7.1	160				5						
30						3	1/2						83	7.1	139		21.0		5 1/2	47.0					
31						3 1/2	1/2						86	7.2	168				5						
4-1						3 1/2	1/2						88	7.1	170		25.0		5 1/2	66.0					
2										2250	30		75	6.7	105				6 1/2						

APPENDIX B-2: page 3 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
3										4000	40		81	7.2	120		28.0		6 1/2	52.0					
4										4500	40	100	82	6.9	80				5						
5										5000	40		95	7.3	85				5			X		X	Temperature, 95°
6													84	8.1	230		38.0		4	62.0		X			Recycle pump off, ? hrs.
7	Off	1	12					150	4	3000	40		85	6.8	65										
8		1	12							4000	40		85	6.6	25		30.0		8 1/2	72.0		X			
9		1	12					150		5000	40		88	6.4	35										
10		1	12							6000	40		88	6.8	70		22.0		9	55.0					
11																									
12																									
13									6	7000	40		90	7.2	60		26.0		9	51.0		X			
14									None				88	6.5	45				7					X	Flow off NaOH, ? hrs.
15									6	5000			90	6.2	50		38.0		9	27.0					
16							2		3	7000	40		92	7.3	77		20.0		8						
17							1		3	7000	40		93	7.1	85		20.0		5 1/2	58.0					Recycle pumps off, ? hrs.
18							2		3	7000	40		93	7.5	170		25.0		4						
19							2			8500	30		90	6.9	57				4 1/2						
20							2		2	10000	40		89	6.9	77		26.0		6	75.0					
21							2		2	12500	40	75	90	6.9	60				5			X			
22							2			5000			93	7.3	100		31.0		5	38.0					
23							2		2	20000	40	70	94	7.3	150				5			X			
24							2						94	7.4	160		24.0		5	50.0					
25									4				94	6.7	55				5						
26							2						94	7.4	105				4 1/2						
27							2		4	17500	40	110	94	7.0	100		22.0	640	5	34.0					
28							2			18000	40		95	7.8	160				4			X			
29							2		5	18000	40	110	97	7.5	163		26.0	380	5	75.0					Recycle pump off, ? hrs.
30							1 1/2		7	18000	40	90	97	7.4	197										
5-1										18500	40		90	7.1	90		25.0	830	4	30.0		X			
2							4			18500	40		84	7.4	200				4			X			

APPENDIX B-2: Page 4 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
3							4			17500	30		84	7.2	125				3 1/2			X			
4							4			17500	30		85	7.3	130		12.0	570	3 1/2	25.0		X			
5							4			18500	40	75	80	6.8	115				6						
6							4					None	86	9.0	1238		15.0	510	5	25.0					
7							4					None	88	8.5	650				4			X			Out of T.B.P.
8							4						88	8.3	530		15.0	610	4 1/2	19.0			X		
9		1	16				4					None	92	8.3	500		11.0								
10			24				4						93	8.1	275				4 1/2						
11		1	24				4						94	7.7	150		1.5	280	7	10.2					
12			24				4					50	95	6.4	45				4 1/2			X			
13			20				2 3/4	100					92	6.4	33		7.5	350	5	15.0					Intermittent caustic addition
14	1												92	8.2	300	68	11.0		6			X			
15							4					None	91	8.2	390		7.0	428	7	17.0					
16							4					None	88	7.8	210		3.0		5	6.5					
17							4						86	7.6	205				5						
18							4						88	7.9	275		5.0	70	4	7.0					Recycle pump off, ? hrs.
19		1	24				4					None	92	7.4	150	3.0	5.0		6 1/2						
20			24				4						91	7.2	100	3.1	3.5	90	9	7.0					Power off, 40 min, emergency air on
21			24				4					75	91	6.3	15	3.1	3.5		11						Intermittent caustic addition
22			24				4					75	91	6.4	35	4.6	4.5	200	15	20.0					Intermittent caustic addition
23			24				4					Yes	92	6.3	35	3.0	4.0		11						
24			24				4			5000		Yes	90	6.6	28	5.3									
25			24				4			5000			91	7.0	16		4.0		6	4.5					
26	1		8				4			1000	40	75	95	6.8	35	3.1	3.5		10						
27							4					None	94	7.6	115		5.0			8.0					
28							4						92	7.5	145	3.1	5.5		4						
29													90	7.8	245	3.1	4.5		4	16.0					

APPENDIX B-2: page 5 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l CaCO3	Dissolved Oxygen, mg/l O2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
30													93	8.0	290	3.1	6.0		5						
31													90	8.0	350	3.1	7.0		4			X			
6-1																									
2		1	24					150					89	7.8	190	3.0	5.0		6						
3			24					150					85	7.9	175		4.0		8						
4			24				4	150					87	8.3	240	3.0			8						
5			12				2	200					90	7.9	240	2	2.5		3	2.5					
6			12				2	200					87	7.6	200				8						
7			12				2	200					92	8.0	200		2.0								
8			12					200					92	8.7	225		1.6		10	1.2					
9			12					200					91	8.1	200				10 1/2						
10			12					200					91	7.9	170		1.2		3 1/2	1.3					
11			12				2	200					93	7.6	103		1.4		4						
12			16				4					Yes	95	7.4	112		1.7			2.6					Caustic feed off 2 hrs.
13			8				3					Yes	95	7.4	83		1.5								Caustic feed off 3 hrs.
14			8				3					Yes	95	6.8	35		5.0		10						
15			12				2					None	96	7.1	80		2.0		10	5.0					
16			12				4			4000	40	50	95	6.5	25		3.5		15						
17			20				2	200				Yes	96	6.9	37	2.0	2.0		13	4.5					
18			24				2	200				Yes	93	6.5	50	3.0	2.0		13						
19			24				2	200		7000	40	100	93	7.4	83	2.4	2.0		15	6.5					
20			24				2	200		9000	40	100	95	7.1	33	2.9			16						
21			24				2	200		1500		100	95	7.0	48				15						
22			26				2	200		9000	20	50	95	6.4	20		1.5		13	5.3					Intermittent caustic addition
23			24				2	200		1500		75	97	6.7	45	3.2	2.5		15						
24			24				2	200		12000	40	75	94	7.2	77	3.0	1.75		20	4.5					
25			24				2	200		1000			95	7.1	100	3.3			25						
26			24				2	200		10000	40	75	93	6.7	45	2.9	2.0		24	6.7					
27			24				2	200		2000		75	94	6.9	100	2.9			15						
28			24				2	200		13000	40	90	95	7.2	90				15						
29			24				2	200		15000	40	100	96	7.4	105	2.3	2.5		19	7.5					
30			24				2	200					95	7.8	66	3.7			23						

APPENDIX B-2: Page 6 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
7-1			24				2	200		12500	40	100	94	7.8	210	2.4	2.5		19	5.5					
2			24				2	200				None	96	9.4	435	2.7			19						Caustic off; High ph
3			24				2	200					96	8.3	180	2.5			19	9.3					
4			24				2	200					97	7.5	80				17						Recycle pump off, ? hrs.
5			24				2	200				Yes	95	7.4	105				17						Caustic feed on 6 hrs.
6			24				2	200				85	93	7.3	90	3.1	2.5		19	4.0					
7	1/4	3/4	24				2	200					96	6.3	25	1.8			16						
8							2			1000			94	6.5	25	2.1	3.5		11						
9							2			12000	40		96	7.2	53	2.0			10						
10							2			1000		48	97	7.0	55	2.4	3.0		10	9.8					
11							2					85	97	6.8	35	2.0			10						
12							2			3000		65	96	6.8	30	2.9			9						
13							2			12000	40	85	95	6.9	35	3.1	2.5			4.0					
14							2			2000		65	95	6.8	45	2.3			14						
15							2			15000	40	60	95	6.8	47	2.7	3.5		12	10.0					
16							2						96	6.9	45				9						
17							2			1500		50	96	6.9	47	2.6	3.0		9	10.0					
18							2			15000	40	50	95	7.3	83				10						Intermittent caustic feed
19							2			500		45	96	6.9	47				9						
20							2			1500		50	96	6.9	40	2.3	3.0		8	10.0					
21							2						97	6.6	53	2.7			11						
22	1/2	1/2					2			1400	40	50	93	6.8	60	2.9	3.0		11	12.0					
23							2						93	7.1	70	2.1			3						
24							2					None	94	8.2	225	3.0	3.0		5	5.3					
25							2					None	94	8.0	245	3.6			5						
26							2					None	94	7.9	235	3.3			5						
27												None													
28							2					None	98	7.7	240	2.9			8						
29		1	16				2					None	96				6.0		10	13.0					
30			16				2	100				None	94	8.0	180	3.5			9						
31			12				2	200				None	94	7.9	145	3.1	4.5		8	10.0					

APPENDIX B-2: page 7 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l CaCO$_3$	Dissolved Oxygen, mg/l O$_2$	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
8-1			12				2	200				None	96	8.0	175	3.3			8						
2			12				2	200				None	97	7.7	120	2.9			8						
3			12				2	200				None	97	7.4	80	3.0	2.5		10	5.0					
4			12				2	200				Yes	97	6.9	50	4.0									Caustic on 4 hrs.
5			12				2	200		5000	40	35	96	6.8	43		2.5			5.0					
6			12				2	200					95	6.4	24	3.1			12						
7			12				2	200					95	6.8	75		2.1		11	5.5					Caustic pump failed
8			12				2	200					95	6.7	45				13						
9		0.9	12				2	200				None	95	6.7	45				13						Sludge recycle rate, .9 gpm.
10			12				2	200				None	95	6.6	20		2.0		3	3.0					
11		0.88	12				2	200				None	98	6.5	55				10						Sludge recycle rate, .9 gmp.
12			8				2	200					93				5.2		10	5.2					
13			8				2	200				None	94	7.0	78				10						
14			12				2	200					97	6.7	30		1.2		3	3.3					
15			12				2	200				None	98	6.6	40				12						
16			12				2	200					96	6.7	15	1.8			14						
17			12				2	200					96	6.6	20	1.2	1.2		14	2.0					
18			12				2	200					96	6.6	15	1.8			15						
19			12				2					125	90	6.4	75	2.2	1.0		31	3.5					
20	0.25	0.75										Yes	94	6.3	20				29						
21							2					None	98	8.7	420	1.8	2.0		5	209.0					
22							2					None	98	8.5	245	2.1			4						Waste feed off, ? hrs.
23							2						98	8.4	205	2.2			4						Waste feed off, ? hrs.
24							2					None	96	8.6	200	1.6	0.9		6	2.1					Waste feed off, ? hrs.
25							2						94	8.2	275		1.0			3.0					
26							2						92	8.0	205		1.25		7	2.5					
27							2						94	7.8	265	2.7			7						
28							2						92	7.8	150	2.6	2.5		6	2.0					

APPENDIX B-2: page 8 of 12

DATE	BIOLOGICAL REACTOR																	Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	CHEMICAL ADDITIVES												MIXED LIQUOR											
	Influent Flow Rates gpm		Daily Dosage							Sodium Hydroxide Feed Solution														
			Pounds					Milliliters		Volumetric Composition														
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
29	0						2						93	7.3	80	3.5			5						No waste flow
30	0						2					None	94	6.7	30	1.3			4						No waste flow
31	0						2					None	95	6.7	20	1.0	3.0		5	5.3					No waste flow
9-1	0.25						2						93	6.5	25	3.0			8						
2										6000	40	120	90	6.1	45		3.0		7	7.5					
3							2			9000	40	125	94	6.7	45	1.9			9						
4							2			12000	40	50	95	7.0	65	2.2	3.5		6	5.5					
5							2			7500		35	94	6.8	40	2.9			6						
6							2			9000	40	125	94	6.3	35		3.5		8						
7	0.25						2			6000			97	8.3	195	1.4	4.0		5	10.0					
8							2			6000	40	160	93	7.0	60	1.8			6						
9							2			9000	40	125	93	6.6	50	2.2	3.0		6	10.0		X			
10							2			9000	40	150	95	7.0	80	2.2			7			X			
11							2			9000	40	155	94	7.2	90	2.0	4.0		6	5.0					
12							2			9000	40	160	94	7.3	88	2.3			6						
13							2			9000	40	155	94	7.2	88				6						
14							2			9000	40	155	95	7.3	125	2.1	4.5		6	10.0					
15							2			9000	40		97	7.4	115	2.8			8			X			
16							2			9000	40	140	93	7.5	165	2.4	4.5		6	15.0					
17									20	9000	40	140	98	7.2	90				7						
18							2			9000	40	135	95	6.9	72	2.2	8.0		6	13.0					
19							2			9000	40	150	96	6.9	80	2.3			5						
20							2			9000	40	150	97	6.9	80	2.7			5						
21							2			10000	40	155	94	7.0	90		14.0			20					
22							2		20	10000	40	155	95	7.0	80				5			X			
23																									
24							2		20	10000	40	140	92	7.8	165				5						
25							2		20	10000	40	150	95	7.0	80		10.0		6	25					
26							2		20	10000	40	160	93	7.0	80				5						
27							2		20	10000	40	155	90	7.0	80				5						
28							2		20	10000	40	150	84	7.1	80		20.0			25					
29							2			9000	40	150	85	7.5	130				6				X		

APPENDIX B-2: page 9 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l CaCO$_3$	Dissolved Oxygen, mg/l O$_2$	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
30							2			9000	40		90	7.3	180		20.0		6	26					Waste feed off, ? hrs.
10-1							2						89	7.2	110				5						Waste feed off, ? hrs.
2							2		20	9000	40	160	89	6.9	70		10.0		5	26					Waste feed off, ? hrs.
3							2		20	9000	40	155	91	6.8	60	2.6			4						
4							2		20	9000	40	165	92	6.8	45	2.2									
5							2		20	9000	40	165	93	6.8	65	2.1	20.0		4	25					
6							2						96	6.8	65		11.0		6						
7							2			12000	50		93	6.6	140	2.7	30.0		6	60					
8							2			9000	40		96	7.1	80		23.0		6						
9			40				2						78	6.8	55		24.0			10					
10			40				2			9000	40	125	81	6.7	50										
11			20				2			9000	40	150	86	6.4	40	4.1			8						
12			33				-		20	9500	40	180	86	6.9	55	2.8	25.0		5	30					
13			33				2		20	10000	40	220	86	6.7	40	2.4			6						
14			20				2		20	10000	40	180	85	6.8	47		15.0			30					
15			20				2			12000	45		88	7.0	57				6						
16			20				2		20	13500	55	180	83	6.8	45	2.7	15.5		6	50					
17			20				2		10	13500	55	180	82	6.8	43				6						
18			20				2			13500	55	180	82	6.9	55	3.1			6						
19			20				2			13500	45	180	83	6.8	50		15.5		6	40.0					
20			20				2			13000	40	180	85	6.7	130		35.0		6						
21			20				2			13500	40	180	83	7.0	185	30	13.0			24.0					Note high ph caused by low Ph$_2$O
22			20				2					None	86	9.6	520	3.8	25.0								
23			20				2		20	12000	40	90	88	7.0	65		10.0		7	20.0					
24			20				2		20	12000	40	150	88	7.1	75				7 1/2						
25			20				2		20	12000	40	150	89	7.3	90		12.0		7						
26			20				2		20	12000	40	165	95	7.3	130		10.5		6	2.5					
27			9.5				2			12000	40		93	6.6	80	3.7	10.0		6						
28			0				2						84	6.7	57	2.8	13.0		6	35.0					Intermittent caustic
29							2			12000	40		80	6.9	67	2.4			6						

APPENDIX B-2: page 10 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l CaCO3	Dissolved Oxygen, mg/l O2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
30			6				2			9000	45		81	7.3	167	2.4	20.0		7	15.5					
31			9				2			12000	40		80	6.7	55				8						
11-1			9				2			13500	40	110	83	6.7	55	2.0			8						
2			9				2			13500	40	115	83	6.9	63	2.6			7	10.0					
3			9				2					None	76	9.4	960	7.2			8	18.0		X			
4			9				2					None	77	8.8	565	3.8			7	15.0					
5			9				2						76	8.4	380	3.9			5						
6			9				2						76	8.1	225	3.4			8						
7			9				2						83	7.5	110	3.4			7						
8			9				2			3000	50	100	88	7.0	55				8						
9			9				2						86	6.8	50	3.3				5.5					
10			9				2			3000	40	100	81	7.0	65	3.9			8						
11			9				2			3000	40	100	82	7.0	58	3.1			8 1/2	5.5					
12			9				2			3000	40	100	81	7.1	67		5.0		7	10.0					
13			9				2			3000	40	80	83	7.0	55	4.5			9	8.5					
14			9				2			3000	40	80	82	7.1	47				9						
15			9				2			3000			77	7.1	63	2.8			9						
16			9				2			3000			74	7.4	97	3.7	5.0		7	8.0					
17			12				2			2000	30	150	80	7.0	60	2.9	5.0		7						
18			12				2			3000	40	150	83	6.8	50	3.1	4.5		7	5.6					
19			8				2			4500	40	125	85	6.6	33	2.4	4.0		8						
20			12				2			5000	40	150	83	6.7	37	3.2	4.5		9	5.4					
21			12				2			7000	45	150	83	6.8	40	2.9	5.0		9						
22			12				2			9000	45	150	88	6.8	42	2.8			10						Waste feed off, ? hrs.
23			12				2			9000	45	150	83	7.1	65		5.0			10.0					Waste feed off, ? hrs.
24			12				2			9000	45	150	73	7.7	170	3.2			10						Waste feed off, ? hrs.
25			9				2					None	75	6.7	35		4.0		10	10.0					
26			12				2			3000	22	100	85	6.9	47	3.1	4.0		10						
27			12				2			6000	40	75	80	6.8	37		3.0		10	5.2					
28			12				2			7500		75	87	6.5	27	3.6	5.3		9						
29			12				2			12000	40	75	89	6.7	37	3.0			9						
30			12				2			7000	45	150	83	7.0	70	3.4	4.5		9	10.0					Aerator off, ? hrs.

APPENDIX B-2: page 11 of 12

DATE	BIOLOGICAL REACTOR																		Sedimentation Tank Secchi Disc. Inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR												
			Daily Dosage							Sodium Hydroxide Feed Solution															
			Pounds					Milliliters		Volumetric Composition															
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l CaCO$_3$	Dissolved Oxygen, mg/l O$_2$	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
12-1			12				2			8000	45	150	88	6.8	45	2.8	4.0		9						
2			12				2			10000	45	150	90	6.8	43	3.0	4.5		19	17.0					
3			12				2			10000	45	150	91	7.0	65	1.8	2.5		20						
4			12				2			10000	45	120	88	6.7	50		4.0		12	5.5					
5			12				2			12000	40	125	87	6.8	53	3.1	4.2		13						Waste feed off, ? hrs.
6			12				2			10000	40	140	88	6.9	57	2.9			11						Recycle pump off, ? hrs.
7			12				2			10000	40	140	81	7.2	102	2.5	4.5		11	5.2					Waste feed off, ? hrs.
8			12				2			10500	45	150	84	6.8	57	4.8			17						
9			3							11000	45	150	86	6.8	57	4.6	5.5		15	10.0					
10							2			11000	40	150	86	6.9	70				11						
11							2			11000	40	130	88	6.9	75	2.5	5.5	220	11	8.0					
12							2			3000	40	130	78	6.4	190	2.7			10						
13							2			7000	45	150	78	6.8	57	2.7			8						
14							2			7500	45	150	78	6.9	65		5.5	480	8	8.0					Waste feed off, ? hrs.
15							2			7000	40	150	81	7.2	88	3.0	4.0	370	10						
16							2			7000	40	150	84	6.9	60	3.0	4.0	160	10	5.0					Waste feed off, 6 1/2 hrs.
17																									
18							2						83	9.4	500	2.9	4.0		10	4.5					Waste feed off, ? hrs.
19							2			3000	45	150	88	6.9	52	3.3	3.5		10						
20							2			3000	45	150	88	6.8	47	3.0	4.5		10						
21							2			4000	45	150	88	6.8	47	3.0	4.0		9	5.0					
22							2			7500	45	150	84	6.8	50	2.4	5.5		9						
23							2			9500	45	150	88	6.8	47	2.8	3.5		9	8.0					Sludge return problem
24							2			9500	45	160	80	7.4	120				9						Waste feed off, ? hrs.
25							2			7500	60	180	82	7.1	80	2.9	4.5		10	10.0					
26							2			8500	50	150	75	7.7	167	2.8	5.5		9						
27							2			9000	45	150	78	7.1	78	2.9			9						

APPENDIX B-2: page 12 of 12

DATE	BIOLOGICAL REACTOR																	Sedimentation Tank Secchi Disc, inches	Return Sludge		Special Conditions			OPERATIONAL NOTES
	Influent Flow Rates gpm		CHEMICAL ADDITIVES										MIXED LIQUOR											
			Daily Dosage																					
			Pounds					Milliliters		Sodium Hydroxide Feed Solution														
										Volumetric Composition														
	Carbonaceous Unit Effluent	Water	Ammonium Sulfate	Limestone	Burnt Lime	Hydrated Lime	Sodium Carbonate	Phosphoric Acid	Tributyl Phosphate	50% NaOH ml.	Water gal.	Feed Rate ml/min	Temperature °F	pH	Alkalinity, mg/l $CaCO_3$	Dissolved Oxygen, mg/l O_2	Imhoff Cone ml/liter	Suspended Solids mg/l		Imhoff Cone ml/liter	Suspended Solids mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
28							2			9500	45	150	83	6.9	58	2.6	7.0		9	8.0					
29							2			10000	45	150	86	7.2	75	2.6	5.5		8						
30							2			10000	45	150	83	7.0	85	2.9	6.8		10	9.0					
31							2			6000	45	150	80	7.2	98	2.4	7.0								
1-1-71							1			6000	45	150	78	6.9	53		5.5		9	6.1					
2										7000	40	145	80	6.9	53	2.9			10						
3										9000	45	150	86	6.7	45		4.5		10						
4										8000	45	125	82	7.1	80		5.0		9	29.0					
5							1			6000	40	145	76	7.0	80		5.5								
6							2						74	7.1	80	2.4	5.0		8	8.0					
7							2						74	6.7	40				7						
8							2					None	74	7.3	90		4.5		7	5.0					
9							2						75	8.0	225	2.8			6						
10							2						83	8.0	205	3.7			4						
11							2						84	7.4	77		3.0		6	8.0					
12							2			3000	40	150	85	7.4	125		4.5		2	8.5					
13							2						91	7.0	25		4.5		8	7.5					
14							2			4000	50	150	92	7.0	70		5.0		2 1/2						
15							2			4000	40	150	91	7.2	83		5.0		7	5.5					
16							2			4000	40	150	85	7.1	70				6						
17							2			5000	45	150	84	7.3	85				7						
18							2			6000	45	150	84	7.2	70		4.5		6 1/2	7.0					

APPENDIX B-3: BIOLOGICAL REMOVAL OF CARBON AND NITROGEN COMPOUNDS FROM COKE PLANT WASTES

Analytical and Operational Data for the Denitrification Unit

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
2-1-70	1		4.6		40	100	80										Added 20 lbs. of sewage sludge to reactor sludge recycle 1 gpm.
2							74		10.0								
3							79		3.0								Recycle pump problem
4			2.3		40		79		21.0			30.0					Sugar concentration reduced
5							90		24.0								
6							77		35.0		5	40.0					
7							74				4 1/4						
8							76				3 1/2						
9							75		30.0		3 1/4	40.0					
10							69				5						
11							78		40.0		3 1/2	40.0					
12							76		40.0		3	40.0					
13							80		40.0			40.0					
14							78		40.0		3	40.0					
15							80		40.0		3	40.0					
16							71		38.0		2 1/2	40.0					
17							69				2 1/2						
18							72		13.0		3 3/4	40.0					
19							79		11.0		5					X	
20							72		36.0		7	40.0					
21							90				5						
22							74		33.0		4 1/2	40.0					
23							72		40.0		4	40.0					
24							73				4						
25							80		32.0		3	40.0					
26							72				3 1/2						2% blow down initiated, to cont. on daily basis
27							71		28.0		4	40.0				X	
28							74				3 1/4						Recycle pump off, ? hrs. Flow off, ? hrs.
3-1							84				3 1/2						
2							78		10.0		3 1/2	15.0					Flow off, ? hrs.
3																	
4							81		10.0		4	13.0					
5			3.5				77	2.6	4.0		4	9.0					Increased B.O.D. feed by 50%

APPENDIX B-3: page 2 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature,°F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
6							81		6.0		4	9.0				X	
7							82				3 1/2						Recycle pump off, ? hrs.
8							78		2.0		3 1/2						
9									2.0		3	2.5					
10							82				4 1/2						Recycle pump off, ? hrs.
11							79		1.5		3	1.8					
12							73										
13							91				10						Blow down halted
14							75				9						Recycle pump off, ? hrs.
15							79				5						
16							80		4.0		3	4.5					
17							84				4						
18							77		5.0		4	5.0					Flow off, ? hrs.
19							87				3 1/2						Recycle pump off, ? hrs.
20							76		1.3		3	1.6					
21							70										Large amount of gas noted during Imhoff cone test
22							71				2						
23							75		.8		2 1/2	1.0					
24							78				3						
25							80		1.0		3	1.75					
26							74				3 1/2						
27							74		2.0		3	5.8					
28							74				3 1/2						
29							74				3 1/2						
30							76		2.5		2	4.5					
31							78				2						
4-1							79		5.0		2 1/2	10.0					Molasses feed started ?
2							78				2						
3							75		6.5		3	4.5					Recycle pump off, ? hrs.
4							77				3						Recycle pump off, ? hrs.
5							85				3						

APPENDIX B-3: page 3 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature,°F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
6							74		20.0		2 1/2	35.0					
7							78										
8							81		14.0		4	26.0		X			Rising sludge noted during Imhoff cone test
9							83										
10							86		1.25		9	2.50					
11																	
12																	
13							84		2.0		4	2.0					
14							82				4					X	
15							82		3.0		4	2.0					
16							86				3					X	
17							88		.05		3 1/2	3.0					Recycle pump off, ? hrs.
18							86				3 1/2						
19							86				3						Recycle pump off, ? hrs.
20							82		1.25		4	1.5					Molasses feed off, ? hrs.
21							84				3						
22							89		2.5		3	3.0					
23							87				3						
24							89		2.0		3 1/2	7.0					
25							89				3						
26							89				3						
27							88		4.0	220	3 1/2	7.5					
28							90				3 1/2						Sludge recycle, 1 gpm; losing solids from clarifier
29							92		2.5	200	3 1/2	1.5					
30							92										
5-1							80		.5	240	3	1.0					
2							80				3						
3							80				3						
4							80		.3	210	2	.5					
5							78				3						
6							82		2.5	180	3	3.5					Increased molasses from 1500 ml to 3000 ml
7							82				2						
8							84		2.5	240	3	3.0					

APPENDIX B-3: page 4 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
9							86										
10				3000	40		88				3						
11				3000	40		90		5.2	210	4	2.0					
12							91				4 1/2						
13							88		6.0	110	3	1.0					
14							87		.031		2 1/2						Baffle installed in clarifier
15							88		6.0	140	3	11.0					Floating solids
16							84				4						
17				3000	40		80				3						
18				3000	40		84		3.5	60	3	4.5					
19							86				3						
20							87	.1	3.5	110	3	5.5					Power off 40 min.
21							87				4						
22							86	.2	1.5	80	3 1/2	1.5					
23							88		5.0		3 1/2					X	Skimmer installed on clarifier; sludge recycle, 1/2 gpm.
24							85										
25							86		2.0		4	2.0					
26							90	.2	3.0		4 1/2						
27							84										Recycle pump off, ? hrs.
28							89		2.5								
29							87		5.5		2	13.0					
30							91		3.5		3						
31							86	.1			3	3.0					
6-i																	Bad odor
2							85	.2			2 1/2						Normal operation
3							82		4.5		2 1/2	15.0					
4							84				1 1/2						Dark color, bad odor
5							84		1.0		3	2.5					
6							85				2						
7							86		.7		2						
8							86		.7		2	.6					
9							88				2						Recycle pump off, ? hrs.

APPENDIX B-3: Page 5 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
10							88		.8		2	3.0					
11							90		.7		1 1/2						
12							91		.7			1.1					
13							93										
14							92		.4		2 1/2						
15							92		.3		2 1/2	.8					
16							92		.5		3 1/2						
17							92	.1	1.0		4	5.5					
18							92	3.0	2.0		5						
19							90		1.0		4	6.5					
20							92				4						
21							92				3						
22							92		.5		3						
23							93	.2	1.0		3						
24							90	1.0	.7		4	2.0					
25							91				3 1/2						
26							90	.5	.5		4						
27							93				4						
28							92				3						
29							93		.5		4						
30							93				4 1/2						
7-1							91		1.0		3 1/2						
2							93				4						
3							92	1.3			4	.7					
4							92				4						
5							92				4						
6							90		1.0		4	2.5					
7							92	.2			3						
8							91	.2	1.25		3						
9							91	.2			3						
10							95		.2		4	1.0					
11							92				4						
12							93				3						
13							91		.3			.5					
14							91	.2			4						
15							91	.2	.5		4	1.0					
16							93				3						
17							92		1.0		3	2.0					
18							92				3						
19							92				3					X	
20							91		1.0		3	1.2					

APPENDIX B-3: page 6 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
21							92	.2			4						
22							89		1.0		3	2.5			X		
23							87	3.1			3 1/2						
24							92	.4	1.0		3	3.0					
25							90	.2			4						
26							90	.7			4						
27																	
28							92				3						
29							92		6.0		2 1/2	7.5					
30							90				3 1/2						Waste flow off, ? hrs.
31							92	.02	3.0		4	4.0					
8-1							93				4					X	
2							93				4						
3							93		2.0		4						
4							93										
5							93		10.0			20.0					
6							97				4						
7							93		1.3		4	1.2					
8						150	93				4						
9				3000		150	93				4						
10				3000		125	91		.5		4	.6					
11				3000		140	92				4						
12							90		6.0		4	1.0					
13							90				4						
14				3000		150	98		1.0		4	20.0					
15				3000		150	94				4						
16				3000		150	94				5						
17				3000		150	94		.3		4	.3					
18						17	92				3						Molasses pump off, 4 hrs.
19						150	89	.7	1.0		10	2.5					Intermittent flow rate of molasses
20							93				13						
21				3000		150	94		15.2		2	70.0					
22				3000		150	94				2						
23				3000		150	94				2						
24				3000		150	92		5.0		2	20.2					
25							91		3.5			15.3					Bad odor
26							89		3.0		3 1/2	11.0					

APPENDIX B-3: page 7 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature,°F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
27							89				2 1/2						
28							88		2.5		3	3.0					
29							90				3						
30				3000		150	90				3						
31				3000		150	90		2.0		3	5.4					
9-1							90	.1			3						
2							87		2.0		2 1/2	6.0					
3							92				3						
4							93		2.5		3	4.5					
5							92				3						
6							98.5				3						
7				3000		150	92		0.2								
8							92	1.0			3						
9							93		3.5		2 1/2	11.0					
10							93	1.0			3 1/2						
11							92		1.0		3	4.0					
12							92				3						
13							92				6						
14							92		1.5		3	2.5					
15							93				3						
16									5.0		2	10.0					
17							94				3						
18							92		5.5		3	10.0					
19							93				2						
20							94				2						
21							92		9.5			20.5					
22							94				2						
23																	
24							89				2				X		
25							92		2.5		2	20.0			X		
26							90				3						
27							87										
28							82		3			15.0					
29							83				2						
30							85		4.5		2	23.0					
10-1							84				2				X		
2							86		3		2	20.0					
3							88				2						
4							89										
5							90		4		2	15.0					
6							92				2						

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
7							89	.1	2.5		2	13.0			X		
8							92		2						X		
9				4500	40		79		2			3.5					Note molasses change
10							78										
11							82	.1			2 1/2						
12							82	.3	5		2	10.0			X		
13							83				2						
14							83		1.5			3.0			X		
15							84				1 1/2				X		
16							80		10.0			30.0			X		
17							78				2						
18							78	.1									
19							80		5.0		2	15.0					
20							82				2						
21							80		5.0			5.0					
22							84		.2								
23							85		6.0		2	23.0					
24							82										
25							85		9.0		1 1/2						
26							86		8.0		1 1/4	20.0					
27							90	.7			2						
28							82	.15	2.5		2	40.0					
29							76	.8			2				X		
30							76		9.0		2	10.0			X		
31							75				2						
11-1							80	.15			1 1/2						
2							80	.15	2.5		2	10.5					
3							72	.5			2 1/2				X		
4							70	.48	1.3		2	4.5					
5				4500			69	2.7			2						
6							71	.16			3						
7							78	.33			2 1/2						
8							83				2 1/2						
9							83		.7			2.0					
10							78	.24			2 1/2			X			
11							76	1.69	.5		3	1.2		X			
12							78		.3		2	.7					
13							76		.9		2	1.5					
14							75				2			X			Color change, light to dark

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature, °F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
15				4500			71				2						Color change, dark to light
16				4500			65		4.0		2	30.0					
17				3000		150	73	.16			1 1/2						
18							78	.30	15.0		2	40.0					
19							79				2						
20							80	.38	3.0		2	4.0			X		
21							78	.98			2 1/2				X		
22							81	.8			2 1/2						
23							77		4.5			10.0			X		
24							67	.2			2 1/2				X		
25							66		.7		3	3.5					
26							77	.3	.3		2						
27							79		.5		3	3.0					
28							81	.5			3						
29							84	.8			3				X		
30							80	.34	4.5		3	1.5			X		
12-1							83				3				X		
2							85		.5		3	1.0			X		
3							86				3				X		
4							86		1.2		2 1/2	3.5			X		
5							84	.79	.7		2				X		
6				4500			84	.1			2						
7				4500			76		.8		2	1.5					
8							79				3				X		
9							81	.5	2.0		2 1/2	4.0					
10							82				3						
11							83	.14	1.0	160	3	3.5					
12							72				3						Waste feed off, 7 hrs.
13							72	.7			3				X		
14							69		.7	70	3	1.5					
15							74	.1	2.5	120	3						
16							78		.7	110	2	.7					
17																	
18							76	.15	3.0			9.0					Sludge return problems
19							80	.16	2.5		3						
20							80		3.0		3				X		
21							82	.1	2.5			2.0			X		
22							83	.14	1.0		3						

APPENDIX B-3: page 10 of 10

DATE	BIOLOGICAL REACTOR										Sedimentation Tank Secchi Disc, inches	RETURN SLUDGE		SPECIAL CONDITIONS			OPERATIONAL NOTES
	Influent Flow Rates, gpm		Additives, Working Solutions				Mixed Liquor										
	Nitrification Unit Effluent	Water	Sugar, pounds	Molasses, milliliters	Water, gals.	Feed Rate, ml/min.	Temperature,°F	Dissolved Oxygen, mg/l O_2	Imhoff Cone, ml/liter	Suspended Solids mg/l		Imhoff Cone, ml/liter	Suspended Solids, mg/l	Foaming Reactor	Sludge Bulking	Floating Sludge Clarifier	
23							82	.7	1.0		3	1.0			X		
24							73				3						
25							76	.17	1.0			1.0			X		
26							70		2.0								
27							70	.17							X		
28							76	.2	.5		3	.5			X		
29							80		1.0								
30							76	1.3	.5		3	1.0					
31							73	.17	1.0								
1-1-71							70		.6		2 1/2	1.1					
2							74	.2			2 1/2						
3							80				2 1/2						
4							73		4.5		2	3.5					
5							68										
6							67		1.0		2	4.5					
7							64				7						
8							66		.2		2	.5					
9							64	.18			2						
10				0		0	75	.5			3						
11							79		.7		3	.9					
12							78				4						
13							83		1.25		4	1.5					
14							85				4						
15							87		.5		3	2.0					
16							78				2			X			
17							78				2						
18							78		1.1		2	2.0					

APPENDIX C

ALKALINITY BALANCE - NITRIFICATION UNIT

Alkalinity is defined as the capacity of a water to neutralize acid. For most waters, this ability can be expressed by the equation

$$\text{Alkalinity, mg/l } CaCO_3 = 50{,}000(2[CO_3^{=}] + [HCO_3^-] + [OH^-] - [H^+]) \qquad (1)$$

where [ ] represents molar concentrations. The purpose of the discussion is to propose a reaction scheme for nitrification and from this scheme calculate potential alkalinity requirements for the process. Verification of the proposed chemical mechanisms will be attempted by making an alkalinity balance on the system which includes, in addition to the biochemical reactions, the supplemental alkalinity intentionally added to the system. In order to accomplish this calculation, the sources and changes in carbonate, bicarbonate, hydroxide, and hydrogen ions must be known or estimated.

The principal reactions taking place within the nitrification unit are the oxidation of ammonia to nitrite and nitrite to nitrate. These two reactions can be represented by the following equations:

$$NH_4^+ + 2H_2O \rightarrow NO_2^- + 8H^+ + 6e^- \qquad (2)$$

and

$$NO_2^- + H_2O \rightarrow NO_3 + 2H^+ + 2e^- \qquad (3)$$

As can be seen, these reactions produce hydrogen ions which are negative alkalinity. These reactions also produce electrons (oxidation) and must be accompanied by simultaneous reactions which utilize electrons (reduction). Two reductive reactions known to occur during nitrification involve oxygen and the utilization of inorganic carbon by the autotrophic bacteria to produce biological cell material. The reduction of oxygen is often represented chemically as

$$O_2 + 2H_2O \rightarrow 4OH^- - 4e^- \qquad (4)$$

The reduction of inorganic carbon, which in this case is present mostly as bicarbonate, to organic carbon is given by equation (5).

$$HCO_3^- + 3H_2O \rightarrow CH_2O + 5OH^- - 4e^- \qquad (5)$$

The hypothetical product, CH_2O, was chosen because it closely approximates chemically the composition of cellular organic carbon. Reactions 4 and 5 produce hydroxide ions which add to the alkalinity but bicarbonate is used in reaction (5) which tends to lower it.

Test data is available which allows at best some approximation of the contribution of reactions (1), (2), and (4) to be made fairly directly. Unfortunately no direct measure of the amount of oxygen utilized in the process was possible. The amount of oxygen utilized can be made indirectly through the use of an oxidation-reduction balance. In other words, the electrons released in reactions (2) and (3) and not utilized by (5) will be assigned to reaction (4), the reduction of oxygen.

To use an oxidation-reduction computation requires the assumption that all significant reactions are known. This assumption is believed to be reasonably valid. Oxidation-reduction balances are best made using the concentration units of equivalents per liter, epl. From the data available, nitrite production, according to reaction (2), was best estimated from the change in ammonia concentration through the unit. Nitrite could not be used directly since the influent was not monitored regularly for this constituent, and variable amounts may well have been present. In addition, some nitrite was converted on to nitrate within the unit. The equivalents per liter (epl) of nitrite produced within the unit is given in equation (6).

$$\mathrm{epl}(NO_2^{-}\text{-}N) = [C_I(NH_3\text{-}N) - C_E(NH_3\text{-}N)]\ \frac{6}{14000} \qquad (6)$$

where,

$\mathrm{epl}(NO_2^{-}\text{-}N)$ = equivalents per liter of nitrite nitrogen,

$C_I(NH_3\text{-}N)$ = influent NH_3 as mg/l - N, and

$C_E(NH_3\text{-}N)$ = effluent NH_3 as mg/l - N.

The factors of 6 and 14000 are, respectively, the electrons released per molecule of nitrite formed or equivalents per mole and the milligrams of nitrite nitrogen per gram mole.

The equivalents of nitrate produced can be estimated directly from the change in concentration of nitrate in the unit. From the stoichiometry of reaction (3), this can be written as

$$\mathrm{epl}(NO_3^{-}N) = [C_E(NO_3^{-}\text{-}N) - C_I(NO_3^{-}\text{-}N)]\ \frac{2}{14000} \qquad (7)$$

The reduction of inorganic carbon according to equation (5) cannot be evaluated from alkalinity measurements for obvious reasons. The alternative is to estimate this reduction through the increase in organic content of the effluent. Two alternate techniques were utilized during the test to monitor this parameter. During the first phase of the experiment, organic carbon measurements were made and the oxidation-reduction statement using organic carbon (OC) becomes

$$epl(HCO_3^-) = [C_E(OC) - C_I(OC)] \frac{4}{12000} \qquad (8)$$

The second part of the test was monitored using chemical oxygen demand and the statement using this parameter is

$$epl(HCO_3^-) = [C_E(COD) - C_I(COD)] \frac{4}{32000} \qquad (8a)$$

The use of either of these methods is not entirely satisfactory as undoubtable losses of these materials occur through normal aerobic biochemical mechanisms and possibly through denitrification in the unit and its sedimentation facility.

The oxygen requirement can be calculated using the fact that the equivalents oxidized must equal equivalents reduced which is

$$epl(oxidized) = epl(reduced) \qquad (9)$$

or

$$epl(NO_2^- -N) + epl(NO_3^- -N) = epl(HCO_3^-) + epl(O_2) \qquad (10)$$

Substituting and reducing equations (6), (7), and (8) gives the oxygen requirement in terms of mg/l of O_2

$$O_2 = \frac{24}{7} [\Delta C(NH_3-N] + \frac{3}{7} [\Delta C(NO_3^- -N)] - \frac{3}{3} [\Delta C(OC)] \qquad (11)$$

for those periods when organic carbon measurements were made and for those periods when chemical oxygen demand was used.

$$O_2 = \frac{24}{7} [\Delta C(NH_3-N)] + \frac{3}{7} [\Delta C(NO_3^- -N)] - \Delta C(COD) \qquad (11a)$$

where ΔC indicates the change in concentration.

The numerical solutions for equations (11) and (11a) for those periods of relatively good nitrification are given in Table C-1. These tabulated results indicate the large amounts of oxygen required by the nitrification unit.

This estimate of oxygen utilization now allows the computation of the alkalinity changes that might be expected during nitrification. Using the definition of alkalinity, equation (1), and the stoichiometry of the major assumed reactions given by equations (2), (3), (4), and (5), the following equations can be derived for alkalinity changes in terms of mg/l $CaCO_3$:

(1) Nitrite production -

$$\text{Alkalinity utilized} = 50{,}000\ [\Delta C(NH_3\text{-}N)]\ \frac{8}{14000} \qquad (12)$$

(2) Nitrate production -

$$\text{Alkalinity utilized} = 50{,}000\ [\Delta C(NO_3^-\text{-}N)]\ \frac{2}{14000} \qquad (13)$$

(3) Inorganic carbon reduction -

(a) For organic carbon

$$\text{Alkalinity produced} = 50{,}000\ [\Delta C(OC)]\ \frac{5}{12000} \qquad (14)$$

(b) For chemical oxygen demand

$$\text{Alkalinity produced} = 50{,}000\ [\Delta C(OC)]\ \frac{5}{32000} \qquad (14a)$$

(4) Oxygen utilization -

$$\text{Alkalinity produced} = 50{,}000\ [CO_2]\ \frac{4}{32000} \qquad (15)$$

The results of each of these alkalinity changes is tabulated in Table C-1. In addition, the algebraic summation of these changes is also given under the column entitled total potential alkalinity utilized. The requirement for alkalinity up to 4500 mg/l must be satisfied or the process will be self-limiting because of low pH and the lack of inorganic carbon. The alkalinity requirement to nitrify the entire waste stream would be very large. In the pilot plant, this alkalinity requirement was met by allowing a decrease in alkalinity through the unit and by addition of soda ash and sodium hydroxide. The total of these alkalinity sources is given in the table.

The difference between the calculated alkalinity utilized, and the alkalinity accounted for by artificial additions and changes in residual alkalinity of the waste are also tabulated as both absolute amounts and as a

APPENDIX C

TABLE C-1: Nitrification Unit, Alkalinity Balance for Selected Sampling Periods

Period	Ammonia mg/l N			Nitrate mg/l N			Chemical Oxygen Demand mg/l O_2			Terms of Equation 11 mg/l O_2			Calculated Oxygen, mg/l	Alkalinity utilized mg/l as $CaCO_3$					Alkalinity Sources mg/l $CaCO_3$			Alkalinity Discrepancy mg/l $CaCO_3$	Percent Error	Comments
	Influent	Effluent	I-E	Influent	Effluent	E-I	Influent	Effluent	E-I	NH_3	NO_3	OC or COD		NH_3 +	NO_3 +	OC or COD -	O_2 -	Total Potential	Waste	Added	Total			
138-144	430	120	310	0	145	145	0	220	220	1060	170	220	1010	8800	1000	1700	6300	1800	200	1200	1400	400	22	Artificial feed
145-151	430	50	380	0	200	200	0	300	300	1300	230	300	1230	10900	1400	2300	7000	3000	100	1600	1700	1300	43	Artificial feed
222-228	580	330	250	0	176	176	440	570	130	860	200	130	930	7100	1300	1000	5800	1600	200	1800	2000	-400	-25	Waste feed
229-235	670	380	290	0	188	188	600	660	60	990	210	60	1140	8300	1300	500	7200	1900	200	1700	1900	0	0	Waste feed
257-263	490	50	440	0	366	366	150	510	360	1510	420	360	1570	12600	2600	2800	9800	2600	100	2500	2600	0	0	Combination
264-270	520	130	390	0	335	335	160	500	340	1340	380	340	1380	11200	2400	3600	8600	2400	200	2100	2300	100	4	Combination
306-312	490	110	380	0	197	197	120	420	300	1300	230	300	1230	10900	1400	2300	7700	2300	200	1600	1800	500	22	Combination
313-319	410	80	330	0	204	204	180	440	260	1130	230	260	1100	9400	1500	2000	6900	2000	200	1800	2000	0	0	Combination
327-333	280	50	230	0	243	243	180	450	270	790	280	270	780	6600	1700	2100	4900	1300	200	1400	1600	300	23	Waste feed

percentage of the alkalinity utilized. This analysis tends to show that alkalinity changes could not be predicted consistently using the reactions involving the oxidation of ammonia to nitrite and nitrate, the reduction of oxygen, and the conversion of inorganic to organic carbon and the monitored data from the experiment. Whether these differences result from assuming an inadequate chemical description of the process or from inadequate data is not known. In large measure, however, these differences may not be unreasonable considering the large multiplication factors applied to a rather limited number of analyses on grab samples in the conversion of these constituents to oxidation-reduction equivalents and to alkalinity equivalents. In addition, these potential discrepancies are magnified through two substractions involved in the computations.

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